Remediation of mixed contaminants (polycyclic aromatic hydrocarbons and heavy metals) in soil with the *S,S*-stereoisomer of ethylenediaminedisuccinic acid and Brij98

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Abstract

The efficiencies of extraction with the [*S,S*]-stereoisomer of ethylenediaminedisuccinic acid ([*S,S*]-EDDS) on selected toxicants were investigated. A soil washing procedure to solubilize mixed contaminants, polycyclic aromatic hydrocarbon (PAH) compounds and heavy metals from soil, into an aqueous mobilizing solution containing 0.1 M EDDS-6% (V/V) Brij98 was optimized and evaluated. The optimized procedure with EDDS had mobilized a total of 101% of B[a]P burden from the soil after nine successive equilibrations with the same charge of mobilization aids (complexing reagent plus surfactant), which was 21% higher than analogous extractions with the equivalent quantity of EDTA and 28% higher than extractions in the absence of complexing reagent (surfactant Brij98 alone). In contrast to B[a]P, chrysene recovery was not affected appreciably by the presence of the EDDS reagent. Modelling of the extraction process for PAH compounds remaining within the soil revealed that B[a]P was extracted more efficiently in the presence of EDDS, *i.e.* the number of washes needed to reduce the initial concentration of B[a]P by half was less than the predicted number of washes in the presence of EDTA or Brij98, and the differences were significant at the 95% level of confidence. EDDS also had an appreciable influence on heavy metal exraction efficiency. Most analyte metals, (Al, As, Cd, Cr, Cu, Fe, Ni, Pb and Zn,) were extracted more efficiently in the presence of EDDS than in the presence of an equivalent quantity of EDTA or in the absence of complexing reagent. By contrast, the mobilization of Ca, Mg, and Mn by EDDS was decreased when compared with EDTA and/or surfactant alone.

Résumé

Les efficacités d'extraction choisis avec le stéréoisomère [*S,S*] – de l'acide éthylènediaminedisuccinique ([*S,S*] - EDDS) sur des produits toxiques sélectionnées ont été étudiées. Un procédé de lavage a été optimisé et évalué pour solubiliser simultanément les composés aromatiques polycycliques de l'hydrocarbure (APH) et les métaux lourds du sol, dans une solution de mobilisation aqueuse contenant 0.1 M EDDS-6% (V/V) Brij98. Le procédé optimisé avec l'agent chélateur EDDS a mobilisé du sol un total de 101% de B [a] P après neuf extractions successifs. Comparativement, quand les expériences ont été réalisée avec EDTA ou sans l'adition d'agent complexant (seulement agent tensio-actif Brij 98), l'EDDS augment la efficacité un 21% par rapport à EDTA et 28% à la solution traitante en absence de agente complexant. Cependant, l'extraction de chrysène n'a pas été sensiblement affectée par la présence du réactif chélateur EDDS. La modélisation du processus d'extraction pour des composés organiques, APH, qui restent dans le sol a indiqué que B [a] P a été extraite plus efficacement en présence d'EDDS, c.-à-d. le nombre de lavages requis pour réduire la concentration initiale de B [a] P à la moitié était moins que le nombre prévu de lavages en présence d'EDTA ou de Brij98 seulement, et les différences étaient significatives au niveau de 95% de la confiance. L'EDDS a également eu une influence appréciable sur l'efficacité d'extraction de métaux lourds. La plupart des métaux analysés, (Al, As, Cd, Cr, Cu, Fe, Ni, Pb et Zn,) ont été extraits plus efficacement en présence d'EDDS qu'en présence d'une quantité équivalente d'EDTA ou en l'absence du réactif complexant. Néanmoins, l'extraction du Ca, du magnésium, et du manganèse par EDDS ont été diminués en comparaison avec seuls l'EDTA et/ou l'agent tensio-actif.

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Chapter 1: Literature Review

1.1. An Introduction to Soil washing

Soil washing is a technology for remediating soils that have been contaminated with heavy metals, persistent organic pollutants (POPs), radioactive materials, or mixtures of these substances. To date, no uniform definition has been advanced for soil washing. The Environmental Protection Agency of the United States of America (US-EPA) considered soil washing to include the entire cleaning process, including soil excavation, above-ground treatment, and re-deposition of the cleaned soil [1]. Most researchers have considered only the above-ground treatment as soil washing, which has consisted of either a physical separation process, a chemical extraction, or a combination of both [2-13]. In this thesis, discussions regarding soil washing have been focused mainly on the chemical extraction using aqueous solutions, but a brief introduction to other types of soil washing (*e.g.* physical separation, organic solvent extraction) has been included.

1.1.1. Physical separation

Soil remediation based on physical separation processes has been developed, in both Europe and North America, principally during the last three decades. It remains a remediation technology that separates contaminants from the soil based on physical characteristics and has been considered to be primarily a particle separation process [5-13]. Seven types of physical separation techniques have been identified: mechanical screening (based on particle size), hydrodynamic classification (based on settling velocity), gravity concentration (based on the density of particles), froth flotation

(based on hydrophobic affinity of the particle surface), magnetic separation (based on magnetic properties of particles), electrostatic separation (based on electrical conductivity properties of particles), and attrition scrubbing (based on mechanical particle-to-particle scrubbing) [3].

Physical separation techniques were primarily applicable to soils that have been contaminated with particulate forms of metals. The choice of technique selected for cleaning depends on: 1) the metal contaminant characteristics (type, concentration, fractionation, and speciation of metals) and 2) the main objective of each technique. Table 1-1 summarizes the basic principle, main objective, and usage of each technique [3].

A single technique of physical separation alone rarely has been adequate to remove metals present in various forms and fractions of the soils. More often, an integrated process train of physical separations was employed. For example, mechanical screening was often used as a preliminary size classification step to provide suitable dimensions of soil particles for further treatment. Attrition scrubbing was employed to remove the metal phase that was weakly bound to the surfaces of particles and to break up soil aggregates. Frequently, this stage was followed by a hydrodynamic segregation to separate the fine fraction from larger sand particles based on velocity or centrifugal force with which particles fall through the water column. In the case of separation of metal-bearing particles from a soil matrix, gravity concentration or froth flotation has been used frequently to separate the fractions. Magnetic and

electrostatic separation techniques have not been used widely due to high capital and operating costs.

Table1-1. Techniques of Physical Separation.

Technique	Separation Principle	Main Objective	Usage
Mechanical screening	Particle size	To provide dimensions of soil particles suitable for further treatment	Widely used
Hydrodynamic classification	Settling velocity or centrifugal force	A size separation method for treating finer particles	Widely used. Not suitable for high clay and/or high humic soils
Gravity concentration	Density of particles	To separate minerals of various densities	Widely used. Not suitable for high clay and/or high humic soils
Froth flotation	Hydrophobic properties of the particle surface	To separate certain minerals from soil by attaching hydrophobic substance from the soil on to air bubbles	Widely used. Chemical additives are required
Magnetic separation	Magnetic properties of particles	To separate minerals of different magnetic properties	Used from time to time. Costs are high
Electrostatic separation	Electrical charge properties of particles	To separate particles possessing different electrical conductivities	Rarely used. Materials must be dry
Attrition scrubbing	Mechanical particle-to-particle scrubbing	To abrade particle surface and to disperse soil aggregates	Widely used

The major limitation of soil washing based on physical separation (SW-PS) was that it was efficient at treating particulate forms of metal-contaminated soils from sites such as military firing ranges, but was less efficient for the remediation of soils with sorbed forms of metals or other types of contaminants such as organics or mixtures of metals and organics [3].

1.1.2. Chemical extraction

Chemical extraction techniques have been efficient when contaminants (metals or organics) were bound to the fine fractions of the soil matrix (clay minerals and soil organic matter), or when the fine fraction made up an elevated percentage of the soil matrix [14].

There were two types of chemical extractions: water based- and organic solvent-based chemical extraction. Organic solvent extraction is applicable primarily to relatively non-polar organic pollutants and most of the solvents that are used are toxic either to soil microorganisms or to plants. Moreover, the use of organic solvents is expensive and frequently represents an appreciable fire hazard.

In this review, only water-based chemical extractions are discussed in detail. Chemical extraction with aqueous solutions – either water-based or water amended with washing additives [4] – have been used extensively to solubilize contaminants (heavy metals, organics, or radioactive materials) from the soil matrix. The washing additives can be either acids, bases/caustic soda, salts, surfactants, chelating reagents,

or combination of these reagents depending on the properties of the contaminants [15-19].

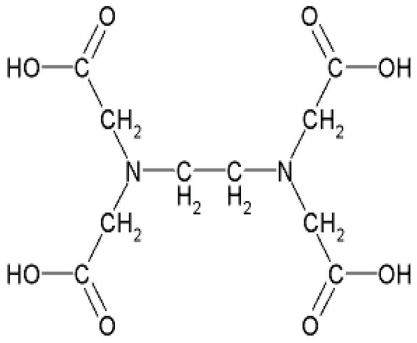
Acid, base or electrolyte-assisted extractions tend to be ineffective in terms of efficiency and cost when compared to chelating agent-assisted extraction [20]. Another undesirable factor is that acid or base-assisted soil washing leaves the treated soil at an extreme pH condition [21] - either too acidic or alkaline to support the growth of microorganism or vegetation. Furthermore, acid or base-assisted soil washing can destroy soil structure and alter the chemical and physical properties of the treated soil [20].

Electrolyte-assisted extraction (*e.g.* $CaCl_2$) or pure water extraction are generally inefficient at removing metals even when they are bound only loosely to soil fractions (*e.g.* forming part of the exchangeable, acid soluble or reducible soil fractions) [20]. Thus, for the remediation of metal-contaminated soil, washing technologies have been focused on chelating reagent-assisted chemical extraction, which represents the most extensively used and the most efficient technology for metal mobilization from the solid phase.

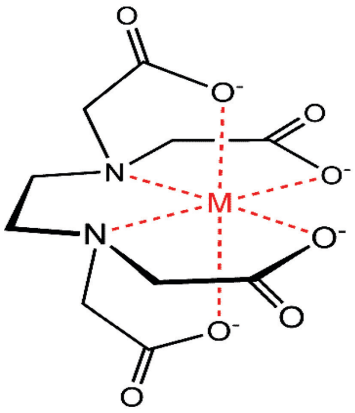
1.1.2.1. Chelating agent-assisted extraction

A chelating reagent is an organic compound containing multiple heteroatoms that are capable of forming several coordinate bonds with a single metal ion. The compound formed by a chelating agent and a metal is called a chelate. A chelating

agent of particular economic significance is ethylenediaminetetraacetic acid (EDTA).



EDTA



Metal-EDTA complex

EDTA is a versatile chelating agent. It forms six bonds with a single metal ion, and it can form stable chelates with main-group cations and less stable chelates with transition-metal cations. EDTA has been used frequently in commercial soap and detergent formulations, because it can remove calcium and magnesium ions (by forming chelates with these ions) that are present in hard water and interfere with the cleaning action of soaps and detergents. In the calcium complex, $[Ca(EDTA)]^{2-}$, EDTA is a hexadentate ligand, and chelation involves the two nitrogen atoms and four oxygen atoms in separate carboxylate ($-COO^-$) groups. EDTA is also used extensively as a stabilizing agent in the food industry. Food spoilage is often promoted by naturally-occurring enzymes that require transition-metal ions as co-factors. These enzymes catalyze the chemical reactions that occur during spoilage. EDTA deactivates these enzymes by removing the metal ions and forming stable chelates. It promotes color retention in dried fruits, vegetables, as well as in canned

or frozen foods. It is also used to improve flavour retention in canned carbonated beverages and salad dressings. In other applications, EDTA is used to separate rare earth elements from each other based on the stability of their EDTA complexes.

In soil washing, the inclusion of chelating reagents in a washing solution can increase the efficiency of soil washing for metal-contaminated soils by desorbing/dissolving metals from metal-containing solid phases (ligand-promoted dissolution of Al, Fe, and Mn from oxide surfaces) and by mobilizing metal ions adsorbed to or precipitated on the surfaces of lattice minerals, or absorbed/bridged within the organic matter fraction) [22-27]. Variables that affect the efficiency of metal removal included the chelant identity and type, solution pH, chelant dosage, reaction time, desorption/resorption rates of metal ions, dissolved organic matter (DOM) [28] and metal speciation within the soil matrix [24].

1.1.2.1.1. Chelating Reagent (Chelant) type

The chelant type is one of the main factors that controls the metal speciation in solution by selectively complexing metal ions according to the magnitude of the stability constants (or conditional stability constants) of their metal-chelant complexes [20]. Metals that form strong/stable complexes with a chelating reagent are selectively mobilized into the solution phase and remain in solution in their complexed forms, which promotes an efficient metal sequestration/removal from the solid phase. On the other hand, less stable complexes of metals readily dissociate if competitive metal ions are present in solution**.** The liberated metals become re-adsorbed on to the solid phase resulting in an inefficient metal extraction[24, 27].

Among chelating agents that have been described in the literature, ethylenediaminetetraacetic acid (EDTA) and the *S,S*-stereoisomer of ethylenediaminedisuccinic acid ([*S,S*]-EDDS, the term "EDDS" will be used in subsequent sections of the text) appear to be among the two most efficient metal chelants [23-34]. So, in this thesis, only EDTA and EDDS are discussed in detail.

In general, EDTA has been demonstrated to be capable of complexing main-group metals whereas EDDS appeared to be superior to EDTA for complexing transition metals selectively [30]. In terms of selectivity, Ca is favourably complexed by EDTA, followed by Mg, Zn, Cu, Pb and then Cd. EDTA is somewhat less efficient at complexing Fe, As or Cr [20, 29-30]. For example, Polettini *et al*. demonstrated that Ca-EDTA was the dominant specie in EDTA extracts, accounting for 50%-60% of the total of EDTA complexes [23]. EDDS has been observed to be very efficient at complexing Cu and Fe, as well as Al (within a restricted pH range) [31, 40], fairly efficient for Zn, Ni, Pb, and As [31], less efficient for Mn, Cr and Cd [40] and inefficient for Ca and Mg [31]. Koopmans *et al.* [28] observed that in certain soil extracts with EDDS, Cu accounted for 80–91% of the total EDDS complexes and in other extracts with EDDS, an increased efficiency for Fe (50%) or Al (37%) was observed. The increased complexing power of EDDS for Cu or Fe has also been observed by other researchers [35, 40]. In the case of Ca and Mg, Tandy *et al*. [31] stated that "despite the high concentrations of Ca and Mg in solution they played a limited role in EDDS speciation as the majority of these ions remained in the free form". Polettini *et al*. [23] observed the same phenomenon: "Ca complex accounted for only a minor portion of total chelant in solution (with Ca in solution being

mainly in the form of free Ca^{2+} ion)" and "only at pH 8, did EDDS speciate appreciably as Ca complexes, with Ca-EDDS accounting for about 20% of total EDDS load."

The avidity of EDDS for metals has been observed to follow the order: Fe > Cu > Ni > Zn > Pb > Cd≈Cr > Mn > Mg > Ca, which can be explained by EDDS complex stability constants reported in Table 1-2 [31]. In general, it can also be inferred that all metal-EDDS complexes are more stable at low pH than that at high pH. As examples, logK $[CuH_2EDDS]$ > logK $[CuHEDDS]^-$ > logK $[CuEDDS]^{2-}$ >> logK $[Cu[OH]EDDS]^{3-}$. The same is true for Ni, Zn, and Al, although the Al-EDDS stability constants have not been listed here (they are to be provided in a later section).

Table 1-2. EDDS complex formation constants.

Complex	LogK	Complex	LogK	Complex	LogK	Complex	LogK
$[Fe(III)EDDS]^-$	23.68						
$[CuEDDS]^{2-}$	20.46	$[CuHEDDS]^-$	24.39	$[CuH_2EDDS]$	26.80	$[Cu(OH)EDDS]^{3-}$	8.81
$[NiEDDS]^{2-}$	18.50	$[NiHEDDS]^-$	21.78				
$[ZnEDDS]^{2-}$	15.34	$[ZnHEDDS]^-$	19.34				
$[PbEDDS]^{2-}$	14.46						
$[CdEDDS]^{2-}$	12.70						
$[CrEDDS]^-$	11.10						
$[MnEDDS]^{2-}$	10.77						
$[MgEDDS]^{2-}$	7.77						
$[CaEDDS]^{2-}$	6.34						

For EDTA-metal complexes, the stability constants alone seem unable to explain the fact that Ca is complexed efficiently by EDTA, because the stability constant of Ca-EDTA was much lower when compared with other metals such as Fe-EDTA, Cu-EDTA, Pb-EDTA or Zn-EDTA (Table 1-3). Possibly, the conditional stability constants [23] are more suitable for explaining the peculiar phenomena of EDTA-metal complexes. Metal-EDTA complexing capacity is strongly affected by solution conditions such as the solution concentrations of major cations (Ca and Mg), which, in turn, is strongly dependent on the initial metal speciation in the soil, on the solution pH and chelant dosage when compared with EDDS. Apparently, the mechanism of the favourable complexation of Ca by EDTA needs to be investigated further.

Table 1-3. EDTA complex stability constants.

Complex	$[CaEDTA]^{2-}$	$[FeEDTA]^{-}$	$[CuEDTA]^{2-}$	$[ZnEDTA]^{2-}$	$[PbEDTA]^{2-}$
LogK	12.44	25.2	18.78	18.00	19.71

1.1.2.1.2. Solution pH

The pH is the factor that most strongly influences the efficiency of chelating agent-assisted soil washing efficiency. As suggested earlier, two basic mechanisms, dissolution and mobilization, simultaneously take place during the process of chelating agent-assisted extraction. The pH appreciably influences both the dissolution and mobilization processes by influencing: 1) The solubility of Al, Fe, or Mn oxy(hydroxides), as well as the solubilities of Ca and Mg minerals that govern the major cation concentrations in solution and influence their complexing avidities

with the chelating reagent. 2) The adsorption and desorption behaviour of metal ions, free chelants, and metal-chelant complexes. Adsorption of any form of the metal or the chelating reagent affects the metal removal efficiency adversely. 3) The stabilities of metal-chelant complexes that influence metal speciation and chelating agent-assisted soil washing efficiency. 4) Dissolution of soil organic matter, which functions as a competing chelating reagent in solution and forms strong complexes with certain metal ions (such as Cu, Fe or Al). 5) The formation of hydroxide colloidal suspensions, which can be appreciable for Al and Fe. As suggested earlier, two fundamental mechanisms, dissolution and mobilization, simultaneously take place during the process of chelating agent-assisted extraction. The influence of each of the factors is discussed in greater detail in subsequent sections.

1.1.2.1.2.1 pH effects on major cation dissolution

Major cations (Ca, Mg, Fe, Al, and Mn) that result from the dissolution of carbonates or oxides can affect trace metal removal adversely as a result of their increased quantities in the soil solution coupled with their avidity for certain chelating reagents (Ca *vs*. Mg avidity for EDTA or Fe *vs*. Al avidity for EDDS). Thus, a successful soil washing technique should possess the following characteristics: a minimum dissolution of major cations and a maximum mobilization of targeted heavy metals which implies that the dominant metal-chelant complexes in solution should be composed of target metal complexes whereas the complexes formed with major cations should be minimal or negligible. The dissolution process is strongly pH dependent. In general, a low pH promotes dissolution of the major cations whereas a high pH inhibits this process. According

to Polettini *et al.* [21], the mechanism of ligand-promoted dissolution of major cations is as follows: "as H^+ ion concentration increases, the particle surface becomes increasingly protonated and acquires a positive charge, thus promoting sorption of negatively charged species including most metal-chelant complexes." Tsang *et al*. [27] stated "If the adsorbed complexes are mononuclear, the process can destabilize the metal-oxygen bond at mineral surfaces, promoting the detachment of minerals into the solution phase."

The extent of dissolution increases with decreasing pH for EDTA-promoted dissolution due to the fact that the adsorption of EDTA and metal-EDTA complexes becomes less prevalent at lower pH; whereas the dissolution by EDDS appears to favour the opposite direction. Dissolved Fe concentration (with EDDS) increases with increasing pH in the range of 4-7 [35] and the dissolution reaches a maximum at pH 8 [23, 26]. In contrast, for EDTA extracts, the highest dissolution of Fe occurs at a much lower pH value (pH 5) [23]. Komarek *et al.* [35] interpreted this phenomenon as: "the higher dissolution of Fe at higher pH values (by EDDS) can be explained by increased detachment of the Fe-EDDS complex due to the higher stability of the complex at higher pH values". Other researchers have attributed this phenomenon to the increased complexing capacity of DOM for Fe at higher pH values [26]. DOM mainly consists of fulvic and humic acids and is a powerful chelating agent for the complexation of Fe [26]. The release of soil organic matter (SOM) is controlled mainly by pH. A higher pH promotes the dissolution of SOM [37] and consequently increases the concentration of DOM in solution. In fact, at pH 8, Fe has been reported to be mainly in the forms of Fe-DOM complexes and colloidal $Fe(OH)_3$.

For Al, in addition to the Al-chelant complex, Al-DOM and colloidal $Al(OH)_3$ exist in appreciable proportions. In addition, hydrolyzed species also contribute appreciably to the variety of Al-species at pH 8 [26, 27]. So the competitive effect induced by a limited amount of available Fe and Al on metal extraction is negligible which, to a great extent, liberates EDDS and enables it to readsorb onto the soil solid phase and aids in the dissolution of more Fe/Al and organic matter. This process is accompanied by the release of metals bound to organic matter (OM), metals bridged between OM and Fe-oxyhydroxides, and metals bound solely to soil Fe-oxyhydroxides [25, 37]. This mechanism accounted for the high mobilization rate of target metals by EDDS at more alkaline pH values.

Although EDTA and EDDS are affected differently by solution pH in terms of major cations in solution, the increased mobilization for target metals all occur at higher pH values. As Nowack *et al*. [24] stated**,** at low pH, the formation of major cation complexes was the dominant process. As a result, remobilization of target metals was possible only at high pH. It should be pointed out that in the presence of DOM in solution, EDDS does not fall completely within Nowack's theory regarding the dissolution of major cations. However, the observed remobilization of target metals is still in accord with these concepts. The reason for this is that at higher pH, major cations (Fe and Al) do not compete successfully with target metals for EDDS but they remained in the form of DOM complexes or colloidal hydroxides and promoted a high degree of target metal complexation and remobilization.

1.1.2.1.2.2. The effect of pH on the desorption/readsorption of metal ion, chelant and complexes

Metal mobilizations can be represented by equilibrium processes between desorption and adsorption of free metal ion, free chelant and the metal-chelant complex. Desorption of any of the forms of the metal or chelant (free metal ion, free chelant or metal-chelant complex) increases the efficiency of the metal remediation process. In contrast**,** adsorption of any of the forms decreases the efficiency of the soil washing treatment. So, examining the factors that influence the adsorption/desorption process can lead to a more complete understanding of the chelating agent-assisted soil washing process. In general, at low pH, both EDTA and EDDS as well as their metal-complexes tend to adsorb on to the solid phases. At higher pH, the adsorption is appreciably decreased [26–28]. For instance, at pH 8, Pb-EDTA does not adsorb on to iron oxide and the adsorption of Fe-EDTA on to goethite accounted for only 6% of the total Fe-EDTA [24]. Similar results have been observed by Koopmans *et al*. [28]. At low pH (< 5), 17% of EDDS was lost from the solution due to binding of EDDS or metal-EDDS complexes onto the soil solid phase whereas at pH ≥ 6, the adsorption of EDDS or metal-EDDS onto solid phase was negligible. Yip *et al*. [26] also reported a similar phenomena: at pH < 4, EDDS adsorption was dominant but if pH increased from 5.5 to 8, adsorbed EDDS decreased from 28 mmol kg^{-1} (20.1% of total EDDS) to 4 mmol kg^{-1} (2.8%). These results demonstrated clearly that EDDS and EDTA adsorption is inversely correlated to solution pH and can be explained by the well-recognized ligand adsorption behaviour: at lower pH, the surfaces of solid particles become increasingly

protonated (a greater proportion became positively charged), which promotes the adsorption of negatively charged species such as EDTA, EDDS, and their metal-complexes.

In addition to the identities of the free chelants and metal-chelant complexes, the pH also has a pronounced influence on the adsorption of metal ions, but in the opposite direction. A low pH reduces adsorption; whereas at high pH**,** adsorption is increased. At pHs above 7, Zn is fully adsorbed. If the pH is increased from 5 to 7, the adsorption of Zn^{2+} increases almost linearly and for pH below 5, Zn^{2+} adsorption is negligible [23]. Nowack *et al.* [24] also reported that at pH 8, 95% of the Zn was adsorbed onto hydrous ferric oxide (HFO) or goethite. In contrast to the fate of the Zn ion, Zn-EDTA complex does not absorb on to HFO or goethite at the same pH value. A similar adsorption behaviour was found for Pb. At pH 5.5, Pb^{2+} adsorption was negligible whereas at pH 8, almost 100% of Pb^{2+} was adsorbed onto goethite or HFO.

Gondar *et al*. [41] investigated Cu^{2+} adsorption behaviour as a function of pH and stated that if pH decreased by 0.5 units, the adsorption of Cu^{2+} onto the soil solid phase was decreased by 15%. The work of Jonsson *et al.* [42] was in agreement with this observation. In the range of pH $\geq$ 6, 100% of total Cu^{2+} was bound to soil minerals whereas in the range of pH < 5, Cu^{2+} adsorption decreased linearly. The pH-dependence of metal ion adsorption can be explained by the fact that increases in pH decrease proton competition and consequently the soil solid surfaces become increasingly deprotonated, which favours binding of positively charged species [39,

[43]. The efficiency of chelating reagent-assisted soil washing for metal remediation depends primarily on the complexing power of the chelant. Thus, the pH range at which the chelating reagent functions optimally (the least adsorption and the highest mobilization efficiency) matters the most. It is clear that increased solution pH should be considered for maximizing target metal mobilization.

1.1.2.1.2.3 pH effects on the stability of metal-chelant complexes

The stabilities of all metal-chelant complexes are influenced by the pH of the medium, especially in the case of the Al-EDDS complex. The stability of Al-EDDS is very strongly pH dependent. At pH 4, 91% of total Al is in the form of Al-EDDS complex; at pH 5.5, the proportion is decreased to 61%; at pH 7, the proportion is decreased further to 0.2% [35] and became entirely dissociated at pH 8 due to the result of hydroxylation and formation of Al-DOM complexes [26-27]. Similarly, Fe-EDDS appears to be more stable and prevalent at lower pH (4.5-6.0) [28], yet it dissociates readily at higher pH (pH~8) [23], which appreciably affects Fe competitive power for EDDS in the elevated pH range. In terms of arsenic (As) complexation by EDDS, the similar result is observed. The efficiency of As (III) extraction increases from ~5% of total As (III) at pH 8 to ~70% at pH 6 [23]. This phenomenon is considered to be associated with Fe and Al dissolution. The anionic forms of As (III, or V) are unable to form stable chelates with EDDS, so their desorption from the solid phase is not dependent solely on EDDS complexation. To some extent, the release of As into the aqueous solution is the companion process of Fe and Al dissolution, because As is believed to be bound mainly to the surfaces of Fe/Al oxides and clay minerals. The simultaneous release during Fe and Al

dissolution processes is considered to account for the increased release/dissolution of As. Polettini *et al*. [23] observed that the amount of As extracted by EDDS increased with the increasing Fe solubilization from minerals and the amount of As bound to Fe, Al and Mn oxides was appreciably decreased after the soil washing.

In the cases of Zn, Cd or Ni, the favourable pH for complexing by EDDS appears to be higher (within the circum-neutral pH range, ≥ 6) compared with Al-EDDS (pH ~4) or Fe-EDDS (pH ~5) [28]. Perhaps, Cu-EDDS complex is the specie that is least affected by changes in pH. Cu-EDDS complex is prevalent at pHs in the range 5-8 [23] duo to its high affinity for EDDS at various pH values (Table 1-2). It should be noted that the stability of Cu-EDDS complex is also affected by pH in the same way as Fe and Al, but to a lesser extent.

EDTA-metal complex stabilities are also pH dependent. Polettini *et al*. [23] reported that with a low dosage of EDTA (0.02 M), where competition between metals was more important because of the sparing quantity of EDTA (insufficient for all metals to bind), Ca displayed a large competitive capacity to bind with EDTA (~90% of EDTA complexes was in the form of Ca-EDTA) and the stability of Ca-EDTA decreases with the increase of pH from 5 to 8, which was indicated by the remobilization efficiencies of Ca by EDTA at various pH values. Of total Ca in soil, 48% was solubilized/complexed at pH 5, 32% at pH 6, 18% at pH 7, and only 15% at pH 8. A similar tendency was observed for Mg, Pb, Cu, Zn, or As. Only Cd has been reported to behave differently. Cd displayed a decreased pH dependence in

EDTA solution. Other researchers have reported a similar pH effect on EDTA complex stability [24].

In summary, all metal-chelant complexes are more stable at lower pHs and less stable at higher pHs. Various metal ions possessed different pH dependent avidities for a particular chelating reagent, which can be manipulated to minimize competition between major cations and target trace metal ions for binding with the chelating reagent. Because the competition between Fe/Al and other metals for binding with EDDS at acidic pH is an important process in determining the speciation of dissolved metals, the pH of the washing solution needs to be adjusted to an alkaline range to achieve a high efficiency of target metal complexation. In the alkaline pH range, although the dissolution of Fe and Al induced by EDDS reaches a maximum, the competition of Fe and Al for binding avidity to EDDS is much weaker compared with the avidity in acidic solution due to the fact that in alkaline solution, the majority of dissolved Fe and Al is either hydroxylated or complexed by DOM. The competitive effect of Fe/Al at high pH is negligible. Moreover, when compared with lower pH values, the quantities of DOM that are dissolved and bound with trace metals (such as Cu, Zn, Cd, and Ni) is increased considerably at higher pH values [28], adding increased complexing capacity to the chelant sink.

1.1.2.1.2.4 pH effects on dissolved organic matter

The presence of DOM in washing solution is particularly important for EDDS metal extractability[25-28, 31] in that 1) DOM forms stable complexes with major cations (Fe and Al), which, to a great extent, minimizes the adverse effect of competition

between major cations and target trace metal ions for EDDS; 2) the presence of DOM (consisting mainly of fulvic acid (50%) and humic acid (50%) [26]), which are natural chelating agents capable of complexing not only major cations but also target metal ions, adds more capacity of complexation to the solution; 3) some DOM molecules released into the aqueous phase can carry sorbed metal ions with them.

Perhaps, Yang *et al*. [25] was the first group to describe the mechanism of chelating agent-promoted SOM dissolution: "We report here that metal ion chelating agents can also enhance the release of soil organic matter (SOM). Chelating agents can alter the association between SOM and the inorganic matrix or affect the structure of SOM itself. In addition, polyvalent metal ions can act as cross-linking agents of the SOM 'polymer' phase by coordinating to carboxylate or phenolate groups on different strands, increasing the rigidity of the matrix and hence the diffusive resistance of partitioned molecules". By extracting metal ions (including Fe^{3+}, Al^{3+}, Ca^{2+}, Mg^{2+}, Cu^{2+} and Zn^{2+}) either bridged between SOM and minerals or serving as cross-linking agents within the organic phase of humic macromolecules, chelating agents cause SOM release from the solid phase through two pathways. "First, organic colloids or macromolecules bound to the mineral surfaces via metal ions can be released into the aqueous phase", and "second, removal of metal ions functioning as cross-linking agents within SOM can lead to a change in the phase properties of SOM from a more constrained, compact state to a more flexible, open state", resulting in increased mass transfer of organic compounds into the aqueous phase.

A number of publications have reported that the release of SOM by chelating agents is pH dependent, and the DOM concentration in solution increases appreciably in response to a pH increase [31, 37]. Grybos *et al.* [37] described the particular mechanism of SOM release at higher pH: "under basic conditions, (1) deprotonation of the hydroxyl groups at mineral surfaces decreases the positive net surface charge and (2) organic molecules become more electronegative. Thus, mineral surfaces and organic matter (OM) repel each other and DOM is released into solution."

The results of Yang *et al.* [25] clearly demonstrate the desorption of soil organic matter as a function of pH. Figure1-1 presents the pH-dependence of DOM release in the presence of a chelating reagent. The DOM is represented by dissolved natural organic carbon (DNOC) in this graph [25]. It illustrates that a minimal release of DOM occurs at pH 2-3 and maximal release is observed at pH 8. The release of DOM was six-fold greater at pH 8 than at pH 2-3. Other researchers have reported the similar observations [26].

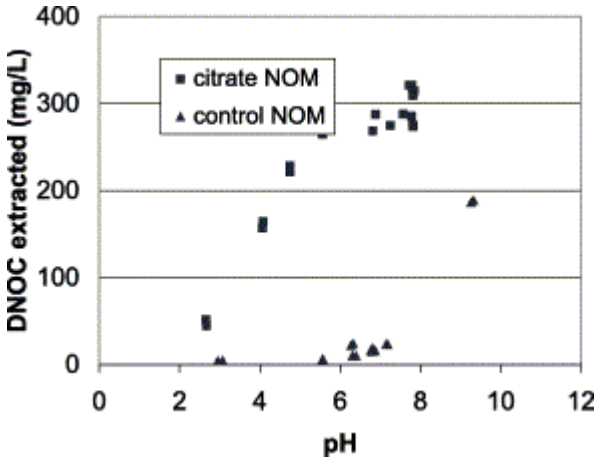


Figure1-1. Desorption of soil organic matter by sodium citrate (0.1 M) as a function of pH.

The pH-dependence of DOM release can also be explained, in part, by the adsorption behaviour of fulvic acid (FA) and humic acid (HA), which represent the two main constituents of DOM. Lippold *et al*. [39] observed that on decreasing the pH, HA became increasingly adsorbed, and at pH 6, HA adsorption was already appreciable. In comparison to HA, the influence of pH on FA adsorption was much less. In other words, the pH-dependence of DOM release has been observed to be associated mainly with desorption of HA at various pH values, which suggests that the increased amount of DOM at higher pH is due mainly to the increased desorption of HA.

Lippold *et al*. [39] reported that HA possessed an increased affinity for polyvalent metal ions (*e.g.* Al^{3+}, Fe^{3+}) relative to FA. Fe bound to HA was observed to comprise more than 90% of total Fe complexes [44], which was one of the reasons why the dissolution of Al and Fe by EDDS was increased appreciably at higher pH values. The higher the pH, the more the HA was release, resulting in increased capacity for complexing Fe and Al leading to increased dissolution of Fe and Al.

Studies have revealed that DOM is a potent competitor to both EDTA and EDDS for metal complexation, especially for Fe, Al, and Cu. Among the metal ions, Fe has the greatest affinity for DOM, followed by Al, and then Cu. Nierop *et al.* [45] reported that even in the presence of a seven-fold excess, Cu wasn't capable of replacing Fe from the Fe-DOM complex**.** Similarly, a three-fold excess of Cu wasn't capable of displacing appreciable quantities of Al from Al-DOM complexes. The explanation of the inability of Cu to affect the interaction between Fe/Al and DOM may reside in

the different affinities of metals for certain functional groups [45]. Fe and Al are believed to bind primarily to phenolic hydroxyl groups, whereas Cu is considered to be bound mainly to carboxylate groups [45, 46]. Among divalent metal ions, Cu forms the strongest complex with DOM. The DOM binding with these metal ions (Fe, Al, and Cu) is so strong that it efficiently displaces both EDDS and EDTA from complexes [31, 38-39]. Tandy *el al*. [31] observed that once equilibrated, Cu-EDTA accounts for less than 1% of total EDTA-complexes due to the presence of natural ligands (DOM) for Cu. Numerous other researchers also observed that at higher pH values, Fe, Al, and Cu complexes are mainly in the form of metal-DOM complexes [25-28, 38-39], because 1) higher pH results in higher DOM concentration, which results in increased capacity of DOM for these metal ions, 2) higher pHs also increase the degree of ionization of binding sites (functional groups) on the DOM molecules, resulting in a net increase in the affinity to bind metal ions. The DOM binding capacity for Cu has been reported to increase two-fold for each unit increase in pH [45]. In addition to a high affinity for Fe, Al, and Cu, fairly high affinities of DOM for Zn, Cd, Ni and Pb in EDDS extracts were also observed [28, 31]. The competitive effects of DOM for both major cations (Fe and Al) and trace metals (Cu, Zn, Ni, Pb, and Cd) resulted in EDDS liberation making it available for binding to other metals. Consequently, the metal-extraction efficiency of EDDS was increased. In the case of EDTA, the effects of DOM were not as pronounced as it was for EDDS. Only at a very low (3.8) pH value, did Ca and Mg form considerable amounts of complexes with DOM [45]. However, at such a low pH, DOM release/desorption was limited, which suggested that the binding capacity of EDTA was hardly increased through

DOM complexation with major cations (Ca and Mg). Thus DOM had little influence on EDTA metal speciation.

As described previously, DOM in soil washing solution plays a beneficial role for metal remediation, although an elevated content of SOM in the soil matrix appears to be problematic (inhibits contaminant removal) for chelating agent-assisted metal removal [29]. DOM complexation is especially important for metal speciation in EDDS extracts at higher pH. This results from an increased efficiency of metal removal by (1) eliminating Fe and Al competition effect (2) adding more complexing capacity to the solution. The three metals with the greatest avidity for DOM are Cu, Fe, and Al, which correspond exactly with EDDS metal avidities. Consequently, a high concentration of DOM present in the washing solution results in an increased capacity of EDDS to complex/mobilize trace metals. This might be the reason why DOM is more beneficial for EDDS-assisted soil washing.

Studies further revealed that the powerful competitive ability of DOM for Al and Fe relied on HA affinity for higher valent metal ions. Lippold *et al*. [39] reported that HA possessed a higher affinity for higher valent metal ions (*e.g.* Al^{3+}, Fe^{3+}) than did FA, and Fe bound to HA was found to be higher than 90% of total complexed Fe [44]. This is one of the reasons why the dissolution of Al and Fe by EDDS is significantly increased with the increasing of pH: the higher the pH, the more the HA is released, the greater the capacity for complexing Fe and Al and the more dissolution of Fe and Al.

1.1.2.1.2.5 pH effects on metal hydroxylation

Hydroxylation has been observed to be one of the major mechanisms accounting for increased Al and Fe dissolution by EDDS at higher pH values. The work of Tsang *et al.* [26, 27] demonstrated that at higher pH (8) and in the presence of EDDS, mineral cations Al and Fe underwent two major changes: 1) they detached from mineral surfaces through metal-exchange by adsorbed metal-EDDS complexes and 2) they became re-complexed by DOM through ligand-competition or formed colloidal precipitates ($Al[OH]_3$ and $Fe[OH]_3$)**.** These changes cause appreciable dissociation of Al/Fe-EDDS complexes and facilitate the process that liberated EDDS can undergo more dissolution cycles of Al and Fe. Thus, at pH 8, the dissolution of Al and Fe reaches a maximum; they present mainly in the forms of DOM complexes or colloidal precipitates. By contrast, the quantities complexed with EDDS are negligible.

1.1.2.1.3. The effect of chelant dosage and the duration of reaction

In addition to solution pH and chelant type, the dosage and duration of reaction have also been observed to affect the extractability of chelating reagent-assisted soil washing. Generally, higher chelant dosage and longer reaction time result in increased metal remobilization. The dosage and time effects vary with respect to metal species. Yip *et al*. [26] studied the dosage effects on EDDS-promoted Cu, Zn, and Pb removal from a field-contaminated soil. In the control extracts, no desorbed Cu or Pb was observed, and only 20% of sorbed Zn was mobilized; under EDDS deficiency (EDDS-to-metal molar ratio of 0.5 in the extracting solution), Cu was the dominant EDDS specie among the three metals due to its highest affinity to EDDS

among all divalent metal ions and the proportion of Cu-EDDS steadily increased with time (from ~60% of sorbed Cu at 3hs to ~75% at 120hs). Zn and Pb were less important in metal-EDDS speciation, and the proportion of Zn-EDDS and Pb-EDDS decreased (from ~55% to 25% of sorbed Zn and 33% to 20% of sorbed Pb) with time due to the competition effect between metals for binding with EDDS, in which some of the EDDS initially bound to Zn and Pb was replaced by Cu. If EDDS was in excess, all three metals Cu, Zn, and Pb displayed increased and similar extraction rates (80-90%) of the sorbed metal forms.

Although increased or excess dosage ensures that there are always sufficient chelating reagents available to the metals of interest, increasing dosage beyond a certain critical concentration does not result in a continued increase in metal extraction efficiency [20]. So, an optimal concentration or dosage is necessary for efficiency and cost [26-28].

The duration of reaction appears to be particularly important for remediation of field-contaminated soils, in which metals are more strongly bound to the reducible or organic matter fractions due to the aging effect [26, 37]. One of the reasons why the reaction time affects metal extractability can be explained by the increased DOM release with time. Figure1-2 presents the DOM desorption and metal mobilization rates as a function of reaction time [37].

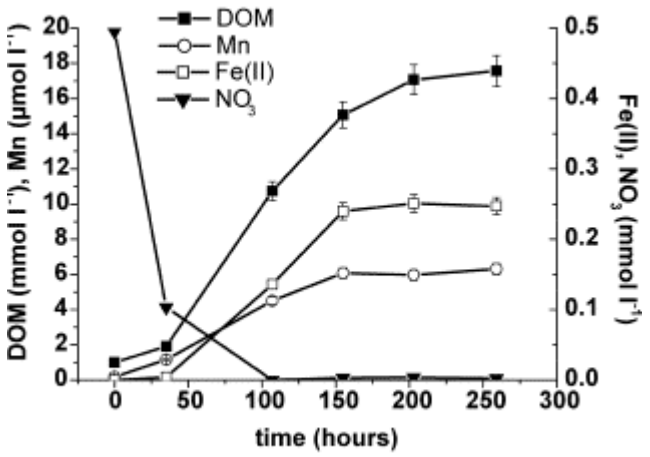


Figure 1-2. DOM release and metal extractability as a function of time.

Two basic mechanisms might account for the increased extractability of metals with time in relation to DOM desorption [43- 44]: 1) DOM plays a role of the metal-carrier during the process of desorption, which indicates that as DOM released into solution, metal ions initially attached to the DOM molecules are released simultaneously into solution; 2) the increased concentration of DOM with time adds extra complexing capacity for metal-binding. As to the mechanism of the time-dependence of DOM release, no clear explanation has been provided so far.

In addition to the terms of "dosage" and "concentration", soil:solution ratio and K_d values (fraction of mass of the metal retained by the soil divided by the mass of soluble metal) have been used frequently to assess the potential mobility of a metal induced by a certain soil washing system [43]. The K_d value is a function of the soil:solution ratio for a particular metal determined for a series of trials performed with the same soil. In general, the smaller the K_d value, the greater the extractability the metal. For the sake of ease of operation, 1:50 or 1:100 of soil:solution ratio has

been used frequently in many studies. However, the work of Yin *et al*. [43] has demonstrated that a lower solids and larger volume of solution did not result in increased metal mobilization at solution pH >7. In turn, smaller K_d values were obtained with larger soil:solution ratios (1:2 – 1:5). Figure 1-3 [43] summarizes the changes in K_d values as a function of soil:solution ratio and pH.

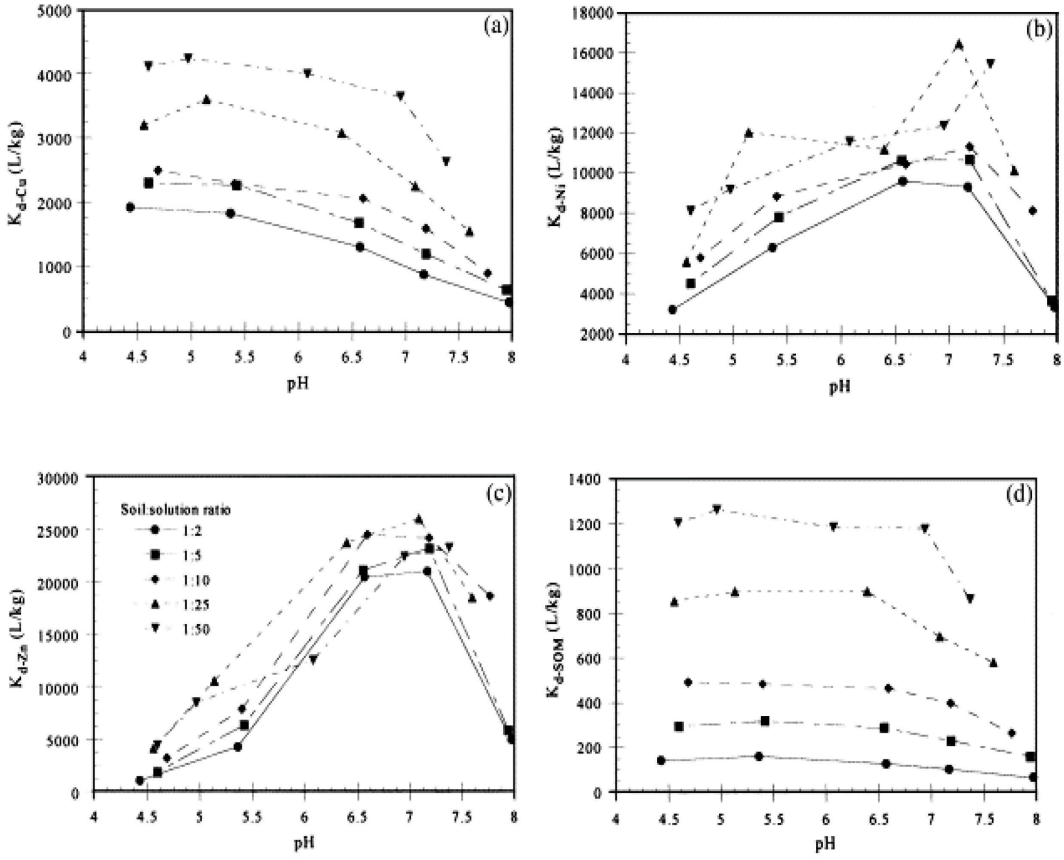


Figure 1-3. K_d values as a function of soil:solution ratio and pH [46].

According to Yin *et al.,* [43], with increasing pH and decreasing solution volume, the surfaces of soil particles were increasingly deprotonated and the repulsion reaction between the negatively charged particles (SOM) was increased dramatically. The decreased space between the soil particles resulted in an increased colloid formation. The colloid was demonstrated to be DOM carrying metal ions. Correlation analysis

indicated that the significant increase in Cu mobilization with decreasing solution volume at high pH was strongly associated with the increased colloid formation of SOM (*i.e.* desorption of SOM). Yin *et al.* also pointed out that the dispersion of particles (colloid formation) was very limited at lower pH values.

1.1.2.1.4. The effect of metal speciation in soil

Metal speciation in soil refers to the metal distribution in different soil fractions, which is affected mainly by the aging process of the soils. The longer the period of time that the soil has been contaminated, the greater the portion of metals that are fused into organic and residual fractions and the more difficult the re-mobilizations the metals become. Several literature reports [31, 36, 47-50] have indicated that for artificially contaminated soils, the majority of the metals remained weakly bound to the exchangeable and carbonate fractions and can be mobilized readily with electrolyte (0.5 M $CaCl_2$). Nearly 45% of Pb and Cd were removed with a single washing from spiked soil whereas for field-contaminated soils, metals tend to bind more strongly to Fe/Mn oxides, organic, and residual fractions. Re-mobilization required more powerful washing solutions that included chelating reagents to achieve satisfactory results. Lim *et al*. [20] stated that metal speciation in soil played an essential role in determining metal extractability by chelating reagents. "Greater than 80% of Cd and 94% of Pb could be removed within 30 min" by EDTA, whereas less than 5% of Cr was extracted due to their different speciation characteristics in soil: "a significant fraction of Pb and Cd were bound to the exchangeable, acid soluble, and reducible phases (68% for Pb, and 62% for Cd)" whereas the majority of Cr was found in the oxidizable and residual fractions

(greater than 82%). Peters *et al*. [29] also reported that metals distributed in amenable fractions (exchangeable, carbonates, and reducible oxides) could be more readily removed by soil washing techniques using chelating reagents compared to those metals that were present in organic and residual fractions.

1.1.2.1.5. The advantages of EDDS over EDTA for soil washing

In soil washing, not only is the metal extractability of a chelating reagent a key factor to be considered, but also the environment effects post soil washing is crucial for the choice of a chelating reagent. Although EDTA had been considered for many years as a powerful, effective chelating reagent in soil remediation, its usage in soil washing has become restricted in many countries and states during the last decade as a result of its adverse environmental effects [30, 31]. Researchers have observed that EDTA is very resistant to biodegradation in soil [51]. The estimated half life can be of the order of years [30, 52-54]. Under natural conditions, EDTA is eventally converted to ethylenediaminetriacetic acid and then cyclized to the diketopiperizide, which accumulates in the environment as a persistent organic pollutant [55]. EDTA residues in "cleaned" soil that was returned to the original site of excavation, generated heavy-metal contaminations in ground and surface waters by complexing and increasing the mobility of these metals within the soil [28, 52, 53]. In addition, its toxicity was found to be moderate to low to most soil microorganisms and plants [52] but it was very harmful to gram negative bacteria causing the destruction of their outer membrane [53].

On the other hand, EDDS possessed promising aspects in both metal extractability and decreased environmental effects. As discussed previously, EDDS has showed equivalent or increased metal extractability in comparison with EDTA. Researches also discovered that EDDS was more rapidly degraded [30, 31, 35, 36] in the environment. An initial lag phase of 7 days was found to be necessary for the population growth of micioorganisms or "adaptation of adequate microbes" [26, 27]. The half-life of EDDS (after the lag phase) in soil varied between 4 to 6 days according to soil type, and it took about 30 days to completely degrade EDDS in soils [31]. Figure 1-4 presents the degradation of EDDS in three different types of soils [31].

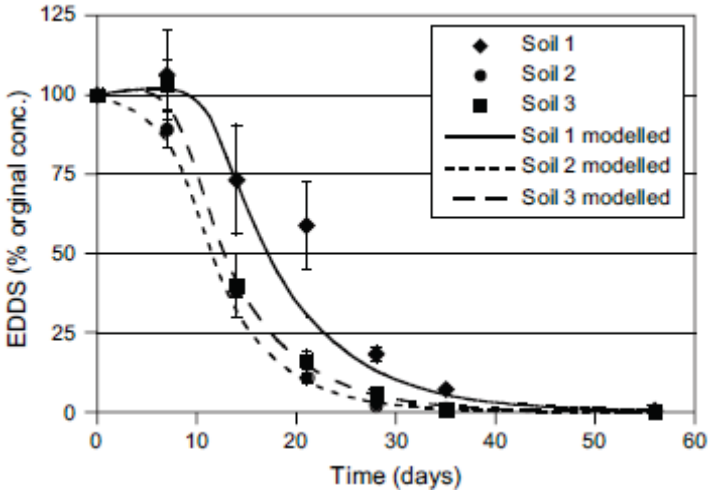


Figure 1-4. The EDDS degradation process followed the first order kinetic after the lag phase**.**

Schowanek *et al.* [52] also investigated the degradation of stereoisomers of EDDS in different environments by means of ^{14}C labelling, and concluded that 1) "the [*S,S*]-isomer is the only fully and practically degradable stereoismer of EDDS" (Figure 1-5); 2) "from an environmental perspective, [*S,S*]-EDDS is the recommended form

for large volume applications, since it is completely degradable in all environmental compartments, and with any innoculum". Figure 1-6 illustrates the degradation of EDDS (indicated by the production of $^{14}CO_2$) in soil was much faster than that in

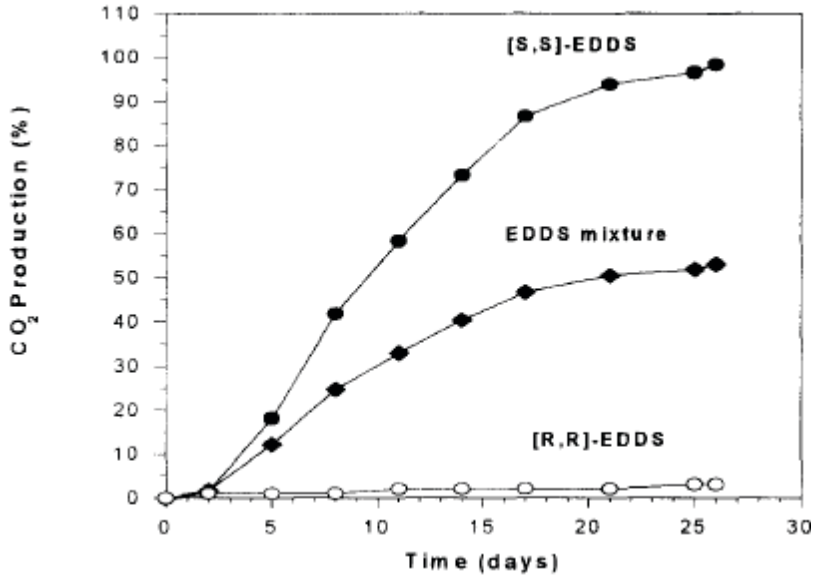


Figure 1-5. Mineralization of [*R,R*], [*S,S*], and mixture of EDDS

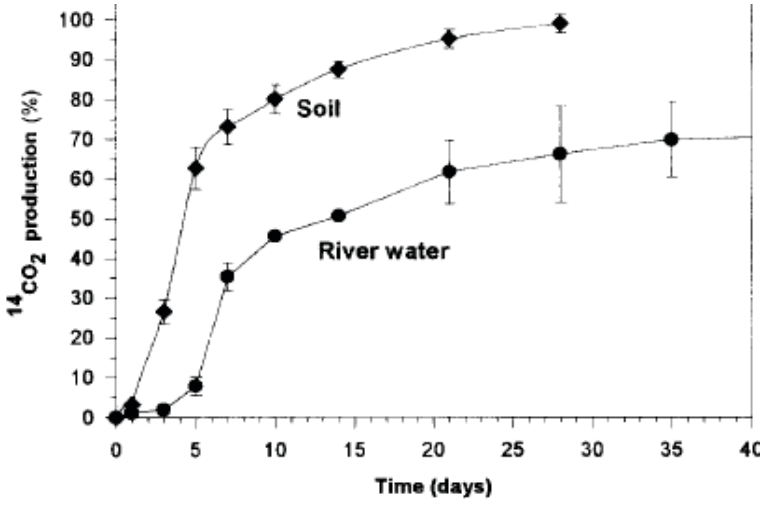


Figure 1-6. Degradation of [*S,S*]-EDDS in soil and river water [52].

river water. The lag phase was less than one day in the tested soil and the half-life was only about 3 days; 90% of EDDS was converted into CO_2 within 15 days [52].

As to the toxicity of EDDS, one study demonstrated that "EDDS revealed a greater toxicity to tobacco (*Nicotiana tabacum*) in comparison to EDTA" [40], but no apparent toxicity to microorganisms" [40, 56-59] or to most other plants [58-60]. In fact, EDDS promoted the population growth of microorganisms, as was revealed through the decreased lag phase for EDDS degradation (the time period necessary (post EDDS addition) for the microorganism population to increase sufficiently to induce rapid degradation of EDDS) [52]. In contrast to EDTA, EDDS is a naturally occurring substance that can be decomposed completely into benign degradation products [56].

1.1.2.2. Surfactant-enhanced soil washing (SESW)

Surfactants (surface-active agents) have been used in soil washing for remediating soils contaminated with organic pollutants, such as petroleum hydrocarbons, polyaromatic hydrocarbons (PAHs), pentachlorophenel (PCP), and pesticides**.** These remediation studies followed soon after the original application was developed in petroleum recovery operations [15]. The effectiveness of surfactant-enhanced soil washing (SESW) has been demonstrated by numerous studies [15-19, 61, 62-65]. The enhanced aqueous solubility of hydrophobic organic compounds (HOCs) resides in the fundamental properties of micellar solubilization.

1.1.2.2.1. The amphiphilic structure and micelllar solubilization

The amphiphilic structure of a surfactant molecule consists of two parts: a hydrophilic head and a hydrophobic tail, which gives the surfactant the ability to form micelles (colloidal-sized clusters) [62]. It is the formation of micelles in aqueous solution that makes surfactants excellent at solubilizing HOCs. At low concentration, surfactants in solution exist as monomers. When the concentration of a surfactant reaches a certain critical value, the monomers form organized aggregates (clusters) with hydrophilic head groups towards the water (solvent) and hydrophobic tails (long carbon chain) located at the center of the clusters. The specific concentration at which micelles start to form is termed the critical micelle concentration (CMC) [62].

Micellar solubilisation is the fundamental property of surfactants, and it occurs when the concentration of surfactants is above the CMC. Studies have showed that the solubility of organic contaminants in micellar solution was greatly enhanced by partitioning hydrophobic molecules into the hydrophobic centres of the micelles [15, 61, 62-65]. The effectiveness of a surfactant in solubilizing a given organic contaminant depends on many factors, but the following sections will only focus on the main factors such as surfactant type, adsorption tendency, and solubilisation capacity.

1.1.2.2.2. Types of surfactants

Based on their origins, surfactants can be classified as synthetic or biosurfactants. Among synthetic surfactants, there are three types of surfactants according to the nature of the hydrophilic head groups: cationic surfactant (with a quaternary

ammonium head), anionic surfactant (a sulphate head, a sulfonate head, or a carboxilate head), and non-ionic surfactant (polyoxyethylene, sucrose, or polypeptide head) [15]. These three types of surfactants have different characteristics on adsorption, CMC value and solubilization capacity, which greatly affect their performance in solubilizing HOCs [62, 63]. In general, cationic surfactants are unsuitable for soil washing. They have a high tendency to sorb to soil particles, causing surfactant loss and resulting in higher concentration needed to form micelles in solution (high CMC values) in comparison to anionic- and non-ionic surfactants [15]. As a result, HOCs removal efficiencies of anionic and non-ionic surfactants in SESW have been extensively studied and reported. The bulk of the literature suggests that non-ionic surfactants are better choices for SESW in comparison to anionic surfactants in terms of washing performance, *i.e.* lower adsorption, lower CMC value, and increased solubilization capacity [62-83].

1.1.2.2.3. Adsorption characteristic

Adsorption of surfactant onto soil surfaces is an undesirable process in soil washing. It results in surfactant loss and reduced performance for the solubilization of organics [63, 66, 67]. Zhu *et al*., [64] stated that micellar solubilization can only occur after the adsorption of surfactant onto soil reaches saturation. Similar observations have been reported by other researchers [17, 63, 83]. The relationship between CMC value and the saturation of surfactant onto soil surfaces for a test surfactant can be observed in Figure 1-7 [63] and Figure 1-8 [64].

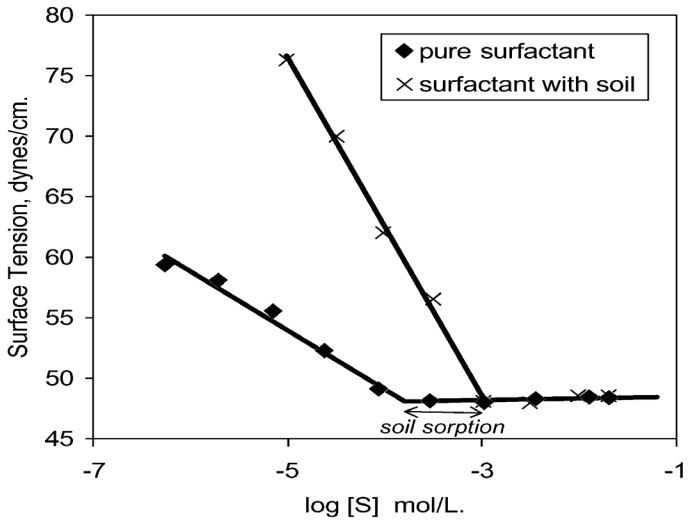


Figure 1-7. Sorption of Brij 35 onto soil [63].

Figure 1-7 indicates that the maximum loss of the surfactant, Brij35, to soil sorption is equal to the difference between the CMC values in the presence/absence of the soil. The two inflection points in Figure 1-7 represent the two CMC values (one for pure aqueous surfactant system, and the other for aqueous surfactant-soil system). For the same surfactant, each system requires the same amount of monomer to reach the CMC value. So, the increased amount of surfactant between surfactant-soil system and pure surfactant system has been lost to the soil. It is clear that in the aqueous surfactant-soil system, CMC is also the saturation point of surfactant adsorption. Above the CMC, additional surfactant molecules remain in the aqueous phase and form micelles [63, 84]. Figure 1-8 [64] reflects the same relationship between CMC and maximum adsorption in a different way. In Figure 1-8, all five non-ionic surfactant**s** are characterized by similar shapes, *i.e.* all the adsorption curves are nonlinear and exhibit a plateau above their CMC value, which indicate that the adsorption of surfactants reach a maximum at their CMC. Similar observations have been reported by other researchers [85-87].

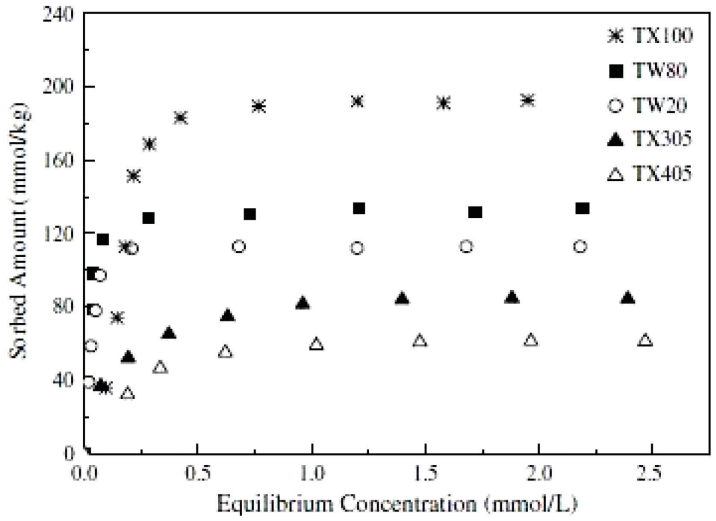


Figure 1-8. The sorption isotherms of non-ionic surfactants onto bentonite [64].

Different types of surfactants exhibit different adsorption characteristics. In general, cationic surfactants show the strongest adsorption tendency among the three categories due to strong interaction between the cationic head groups and the negatively charged soil surfaces [15]**.** By contrast, non-ionic surfactants appear to be the less strongly adsorbed to soil and anionic surfactants are in between [62]. In addition to the adverse effect mentioned earlier, the adsorption of surfactant onto soil also increases the hydrophobicity of soil surfaces, which promotes the re-adsorption of the solubilized organic pollutants onto the soil surfaces and further decreases the efficiency of soil washing [15, 63]. The CMC value is one of the indicators being used to compare the performance of various surfactants. In general, the lower the CMC value of a surfactant, the better its performance. For the same or similar hydrophobic chain lengths (tails are the same or similar), CMC magnitudes are in the order of non-ionic surfactant < anionic surfactant < cationic surfactant. In

other words, non-ionic surfactants possess the highest solubilization capacity for HOCs, and therefore have been used extensively in soil washing studies [62-72].

1.1.2.2.4. Solubilization characteristics

Solubilization of HOCs by surfactants are initiated principally at the CMC and the solubilizing capacity is proportional to the surfactant concentration above the CMC value (Figure 1-9) [62]. Only at concentrations exceeding the CMC, are surfactants able to solubilize HOCs in aqueous solution [62, 63]. At concentrations below the CMC, surfactants not only do not have appreciable ability to solubilize HOCs, but also enhance the adsorption of HOCs onto soil surfaces due to the hemimicelle effect [66, 67].

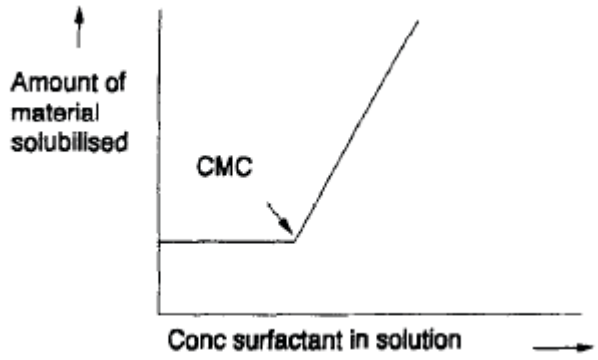


Figure 1-9. Solubilisation of hydrophobic organic materials as a function of surfactant concentration and micelle formation in aqueous solution [62].

As implied by their name, hemimicelles are formed on the surfaces of soil particles in an organized pattern. Cationic surfactants, for example, are strongly adsorbing onto soil surfaces due to the favourable electrostatic interactions between the positively charged head groups of cationic surfactants and the predominately negatively charged soil mineral surfaces. As a result, the molecules of cationic

surfactants form an organized layer with their head groups towards soil and hydrophobic tail groups towards water. This layer of bound surfactant is called hemimicelles [62]. At low concentration, surfactants in the aqueous phase exist as monomers and have little attractive force for HOCs. On other hand, the hydrophobicity of the soil surfaces is increased due to the formation of hemimicelles (all the hydrophobic tails facing the water phase), which attract hydrophobic molecules onto soil surfaces through partitioning process [71, 72]. Based on this description, it can be seen that two basic operational variables, surfactant type and concentration, are the main factors that determine the efficiency of a surfactant-enhanced soil washing (SESW). However, there are other issues that need to be considered in terms of feasibility or practicability when a new SESW technique is envisaged: cost, toxicity, and biodegradability of the selected surfactant [15].

1.1.2.2.5. Newly developed surfactants and their effectiveness in soil washing

The gemini surfactant is a relatively new surfactant group developed in the surfactant industry. Generally, the molecules of gemini consist of two identical surfactant monomers linked by a spacer located in the vicinity of the head groups. The spacer is generally an alkyl group with 2-10 carbon atoms (Figure 1-10) [15]. It is the length of spacer that greatly affects the performance of the gemini surfactant. For cationic gemini surfactant, the longer the length, the less adsorption of the gemini molecule and the better the performance [76]. As for anionic gemini surfactants, the effect of the spacer length is in the opposite direction [15]. So far, no "non-ionic gemini surfactant" has been reported. Instead, zwitterionic surfactant, which is a

combination of one anionic surfactant and one non-ionic surfactant, has been synthesized and investigated [77, 78]. However, due to a limited number of studies, the performance of both anionic gemini and zwitterionic surfactants remains unclear. In short, the cationic gemini surfactants are attracting attention because of their remarkably low CMC values, high solubilization capacity, and consequently superior performances relative to monomeric surfactants [15].

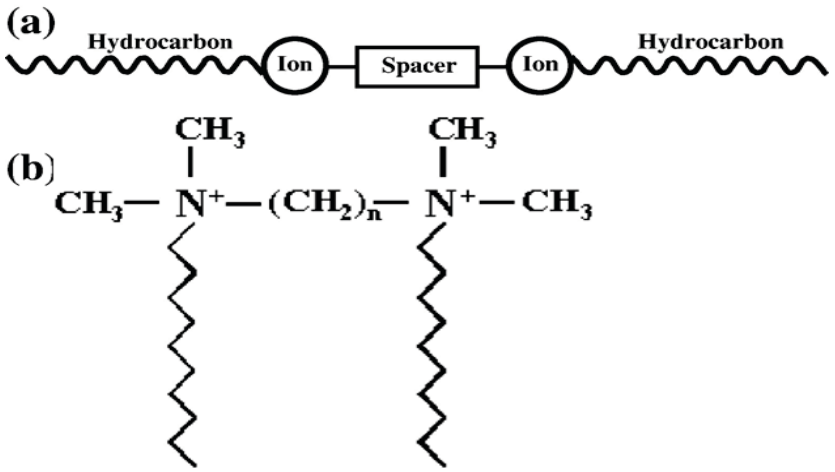


Figure 1-10. (a) Schematic representation of a gemini surfactant, (b) Molecular scheme of a gemini surfactant molecule composed of two identical hydrophilic headgroups and two hydrophobic tail groups [15].

1.1.2.2.6. A mixed surfactant system

Instead of using one single surfactant in soil washing, there has been a tendency to increase soil washing efficiency by using a mixed surfactant system. Usually two opposite types of surfactants are chosen [15]. Although studies are limited on the efficiency of HOC removal by mixed surfactant system, there are some evidences that the mixed surfactant system appears to be superior to any of the corresponding single surfactant systems because of the reduced surfactant adsorption which results in increased HOC removal efficiency [73-75]. For example, in general, anionic

surfactants have appreciably decreased solubilization capacity relative to non-ionic surfactants for HOCs [79, 80], but anionic-nonionic mixed surfactant systems have displayed an increased solubilization capacity relative to the corresponding individuals [81, 82]. Paria *et al*. [15] stated that the mixed surfactant system potentially may be the better system for SESW.

1.2. Soil washing technologies for the removal of polycyclic aromatic hydrocarbons (PAHs)

1.2.1 PAH compounds and their toxicities

PAH compounds represent a group of compounds that possess two or more fused aromatic rings (Figure1-11) [88] formed during the incomplete combustions of organic materials under oxygen deficient conditions [88-90].

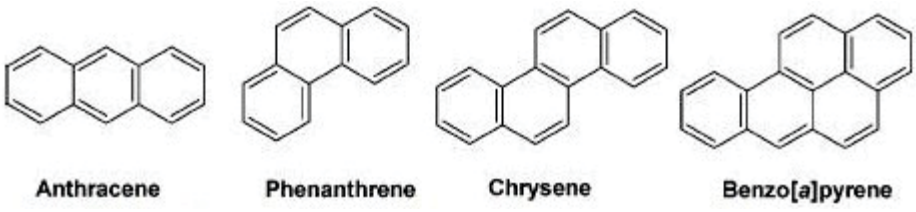


Figure 1-11. Structures of tri-, tetra-, and pentacyclic PAH compounds [88].

PAHs have long been regarded as environmental primary pollutants that induce various degrees of carcinogenesis and mutagenesis in human and animal cells [91-103] through oxidative metabolic activation [93, 103]. Among PAH compounds, benzo[a]pyrene (B[a]P) has a relatively larger molecular size (five fused rings) and possesses the greatest carcinogenicity and mutagenecity. With four fused rings, chrysene (chry) is another PAH that has been studied extensively. Taking B[a]P as

an example, the PAH metabolic pathway in human and animal cells is a multi-step enzyme mediated oxidative activations (Figure 1-12) [93].

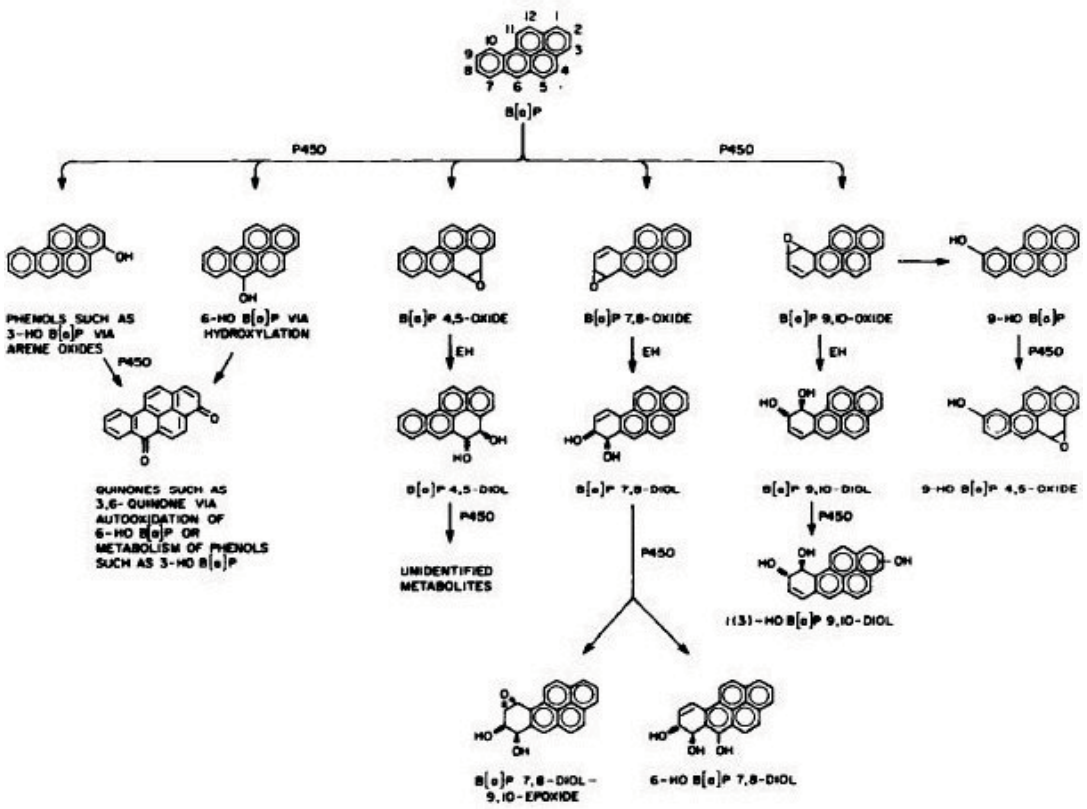


Figure 1-12. Metabolic activation of B[a]P by microsomal cytochrome P-450 and epoxide hydrolase [93].

Although a number of oxidative metabolic pathways have been identified as indicated in Figure 1-12, evidences suggest that the dominant pathway by which B[a]P is converted to an ultimate carcinogen follows three sequential stages (the fourth from the left in Figure 1-12), which are in the order of formation: B[a]P → B[a]P 7,8-oxide → B[a]P 7,8-dihydrodiol → B[a]P 7,8-diol-9,10-epoxide [93]. This pathway can result in four possible stereo-isomers of B[a]P 7,8-diol-9,10-epoxide (Figure 1-13) [93], and all of them result in activation of the bay-region.

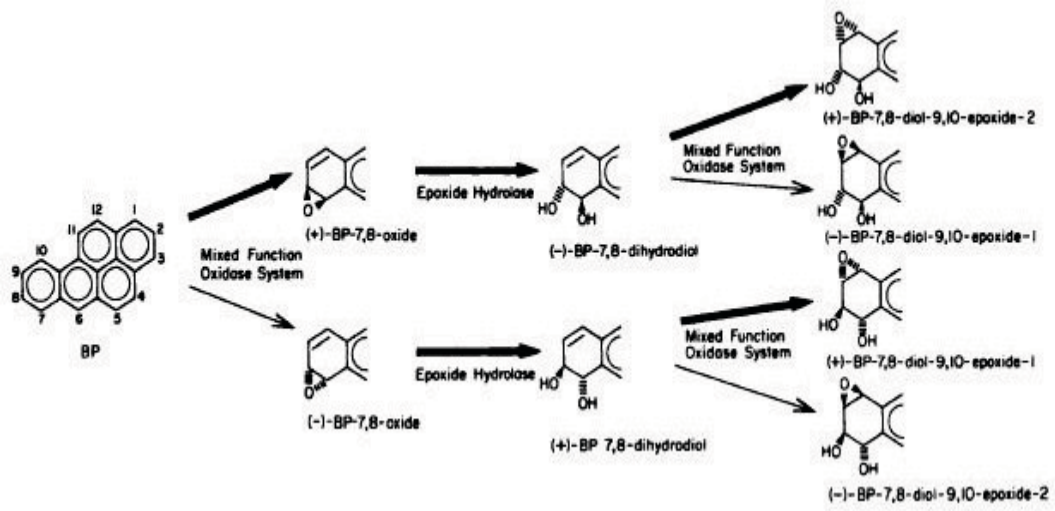


Figure 1-13. An oxidative metabolic pathway of B[a]P resulting in four possible stereo-isomers of 7,8-diol-9,10-epoxide. Bold arrows denote major product of each step. So, (+)-B[a]P-7, 8-diol-9, 10-epoxide-2 is the dominant product of all four isomers [93].

The "bay-region" is defined as follows: "epoxides on saturated, angular benzo-rings, when present in the bay-region of a PAH compound, should possess a uniquely high chemical reactivity" (Figure 1-14)

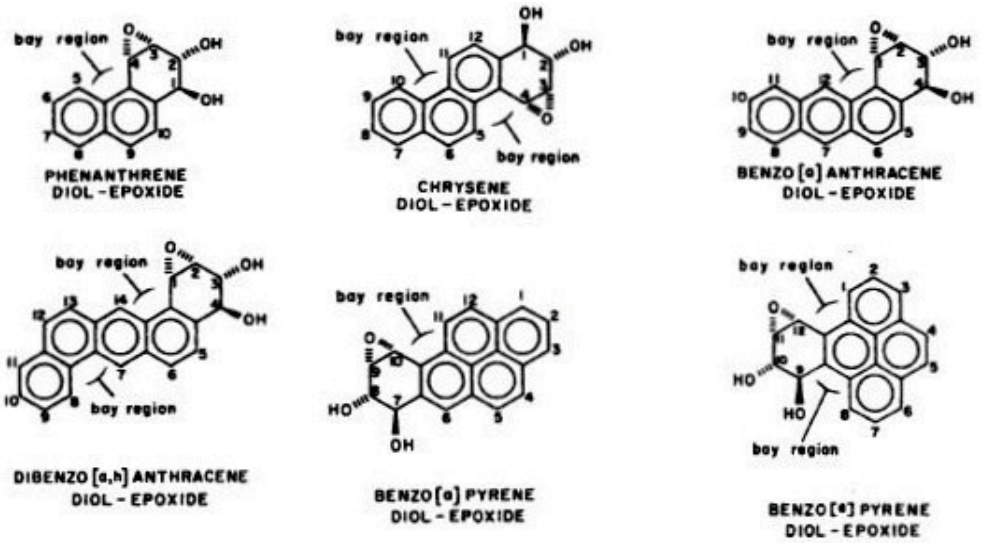


Figure 1-14. Bay-region diol epoxides of several PAH compounds [93].

Studies indicated that the bay-region 7,8-diol-9,10-epoxide resulted from this metabolic pathway, possesses the highest carcinogenicity. It covalently binds to DNA in cells or tissues and results in DNA adduct formation. The covalent linkage was found to be between the benzylic carbon of epoxide (*i.e.* C_d in Figure 1-15) [92] and the amino groups of deoxyadenosine and deoxyguanosine residues in the DNA. Further investigations have revealed that the majority of DNA adduct formations occurred on the deoxyadenosine residue of DNA, which is considered to be the main reaction between the bay-region 7,8-diol-9,10-epoxide of B[a]P and DNA [92]. In short, the carcinogenic activity of B[a]P is based on two series of reactions in human or animal cell. First, B[a]P is converted to bay-region 7,8-diol-9,10-epoxide through oxidative metabolic activation by two enzyme systems: the microsomal cytochrome P-450-dependent monooxygenase system (P-450) and the epoxide hydrolase system. Subsequently, the bay-region 7,8-diol-9,10-epoxide of B[a]P is bound to DNA

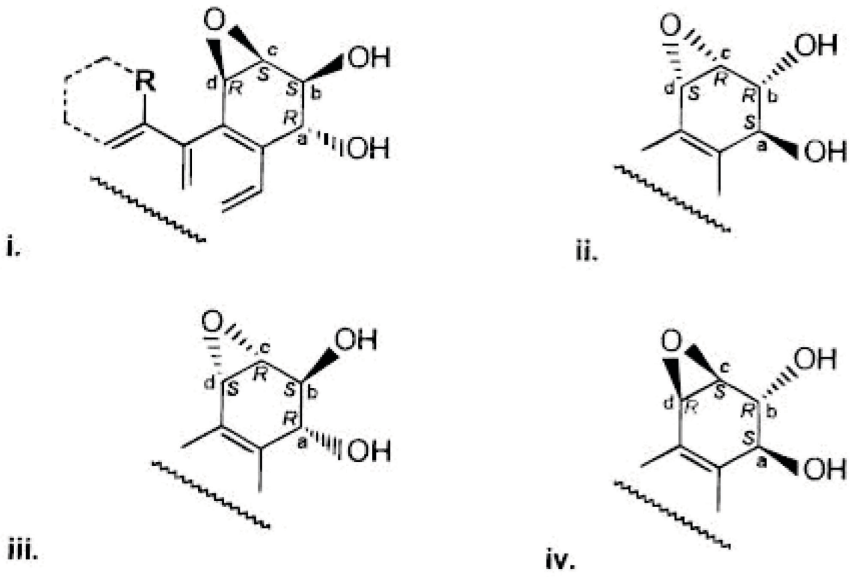


Figure 1-15. Generalized structures of the four configurational isomers of bay-region dihydrodiol epoxides. The benzylic carbon of the epoxide (marked as "d") undergoes electrophilic attack by an amino group of DNA forming an adduct [92].

through a covalent linkage between the benzylic carbon of the epoxide and the amino group of a deoxyadenosine residue of DNA to form DNA adduct which can result in a variety of cancers in human and animals [92-105].

In addition to carcinogenesis, studies have revealed that certain of the B[a]P metabolites (including the bay-region 7,8-diol-9,10-epoxide) also possess varied degrees of mutagenesis. They readily bind to DNA and result in heritable gene mutations [102].

PAHs exist almost everywhere in the environment: air, water, and soil [106-109] due to their diverse sources of formation that include cooking, smoking, vehicle emissions, power plant emissions, coke production, volcano eruptions, and other processes of burning of vegetation, coal, and petroleum [90]. Menichini *et al.* [89] investigated urban air pollution of ~60 towns worldwide, and concluded that all urban airs investigated were polluted with PAH compounds. Individual PAHs were observed in the range of 0.1-100 ng/m^3. In general, air pollution with PAHs was less in North America (individual PAH, 0.1-1 ng/m^3), moderate in Europe (1-50 ng/m^3), and high in Asia (1-100 ng/m^3). Ilnitsky *et al* [90] reported that in the air of smokers' apartments, B[a]P concentration was 3 fold higher than that of non-smokers. Further studies suggested that the indoor B[a]P concentration in non-smokers' apartments can be attributed mainly to vehicular emissions [90]. Size distribution studies revealed that PAHs in air are mainly adsorbed on respirable particles [89, 108], which is responsible for increased lung cancers [95, 99]. As for water pollution, an estimated

total annual release of PAHs into the aquatic environment is 230,000 metric tons [110], which, to some extent, might be responsible for food chain pollution.

Soil, as the ultimate sink of PAH pollution, has been found to be heavily polluted with PAH compounds at such industrial sites as tar ponds, coal storage sites, coke production regions, power plant vicinities and former manufactured gas plant sites [88]. In these polluted sites, individual PAH, benzo[a]pyrene (B[a]P) or chrysene (chry), in soils can reach as high as ~100 mg/kg soil [111], which require efficient, cost effective and environmentally benign techniques to clean-up these pollutants.

1.2.2. Surfactant-enhanced soil washing (SESW) techniques for PAHs removal

Based on the hydrophobic characteristic of PAH compounds, environmental concerns, and economic perspectives, the most extensively studied technique for PAHs removal has been the surfactant-enhanced soil washing (SESW) [62-64, 80-82], which has been characterized by moderate to high efficiency, modest environmental threats, and one of the least expensive remediation techniques to date. Although there are other techniques have also been investigated including hot (sub-critical) water extraction [112], organic solvent/Soxhlet extraction [113-115], supercritical fluid extraction (SFE) [114-117], they have met with less enthusiasm. Organic solvent/Soxhlet extraction has been long regarded as a traditional technique for HOCs removal. However, there are problems with this technique: 1) it requires large volumes of organic solvents [115]; 2) most solvents used are harmful to the

environment [113] and their use can represent an appreciable fire hazard. As a relatively new technique, SFE does not pose any environmental threat and the extraction rates have been demonstrated to be reasonably high. However, the high investment cost of commercial systems represents an appreciable drawback for applications in soil remediation [118]. In this section, the discussion will be focused mainly on SESW.

In general, soil washing performance for PAHs removal is affected by two sets of factors. One group of factors are the intrinsic properties of PAH compounds and the soil matrix where they reside, the other group of factors are related to the soil washing system. All the factors involved in the washing system should be optimized according to the first group of factors, so that an efficient removal of PAHs can be achieved.

1.2.2.1. Properties of PAHs and the soil matrix

The properties of PAHs which influence soil washing performance include the number of fused rings [19], physical location within the soil matrix [47], and chemical interactions with humic substances (HS) [119]. As for the soil matrix, the SOM content and the degree of cross-linking between molecules of HS (*i.e.* FA and HA) are the main factors which affect the efficiency of soil washing [120].

1.2.2.1.1. Intrinsic property and location of PAHs influence the desorption process

The number of fused rings on the target molecule is one of the key factors which significantly affect the performance of SESW. In general, the hydrophobicity of a PAH compound increases with the increasing ring number [19]. Among PAH compounds, B[a]P has an increased ring number (five) and therefore is the more lipophilic compound. Chry is next with four fused rings [111]. The high hydrophobic nature of B[a]P and Chry provides ability to bind more strongly onto the SOM phase than other PAH with fewer rings. They are more resistant to desorption processes and in consequence, result in decreased washing efficiency [121].

The location of PAHs within soil matrix can influence appreciably the efficiency of soil washing. PAHs adsorbed on the surfaces of soil particles (*e.g.* artificially contaminated or freshly contaminated soils) are readily washed off by surfactant micellar solution. In contrast, PAHs located within the three-dimensional structure of SOM due to aging effects (*i.e.* soils being contaminated with PAHs over an extended period of time) are more desorption-resistant [47] because: 1) cross-linked SOM phase serves as natural barrier by blocking the PAHs partitioning pathways ; 2) PAHs located within the inner SOM phase have increased covalent character in their interactions with HA molecules; and 3) the covalent linkages are not readily broken by micellar partitioning forces. Perhaps, high energy contact is needed to break the covalent linkages and to facilitate the PAHs mass transfer from solid phase into aqueous solution. Evidences of covalent bond formation between molecules of HA and PAHs have been provided in the literature by Kacker *et al* [119].

1.2.2.1.2. The Soil matrix

High SOM content has been demonstrated to have an adverse effect on soil washing performance [16, 120]. SOM is generally comprised of FA, HA, and humin substances. Among the three constituents, only FA possesses a higher polarity, whereas both HA and humin are hydrophobic substances, which have high affinity to both PAH compounds [49, 120] and surfactants [122]. As a result, the adsorption of non-ionic surfactants and PAHs onto the soil solid phase is increased with the increasing SOM content [15]. The number of micelles in the washing solution is decreased and the amount of PAHs partitioning into aqueous phase is reduced. Thus, an elevated content of SOM generally results in a decreased washing performance in SESW [16]. This undesirable effect is remarkably high for higher ring PAHs (*e.g.* B[a]P) [120].

In addition, a high degree of cross-linking between SOM molecules further hinders the PAHs mass transfer by impeding partitioning pathways from the solid phase into the aqueous phase. The degree of cross-linking increases with the increasing of SOM content [25].

It should be pointed out that once soil organic matter has dissolved into the aqueous washing solution, it can play two positive roles that enhance the efficiency of PAH removal. The two positive roles of DOM are: 1) it serves as natural surfactant (*i.e.* FA and HA) to increase the micellar capacity of the surfactant-based washing solution aiding in the PAHs partitioning process [123]; 2) it can also function as a chelating reagent to increase the complexing capacity of the washing solution. This helps to keep the dissolved metal ions in solution and increases metal ion removal

from the solid phase [25]. In short, DOM in washing solution is beneficial in two ways: increasing PAHs solubility as well as metal removal efficiency. The positive effects of DOM on soil washing performance have been well established by numerous studies [47, 49, 121, 123-126].

1.2.2.2. Operational variables in the soil washing system

The operational variables of soil washing system are chosen according to the intrinsic properties of the target PAH compounds and the soil matrix, including surfactant selection, concentration, solution to soil ratio optimization and additional aids that can added to the washing solution.

1.2.2.2.1. Surfactant selection

The selection of a suitable surfactant includes three considerations: adsorption, toxicity, and biodegradability. An ideal surfactant used in SESW should possess the following characteristics: lower adsorption/CMC value, non-toxic, and an elevated rate of biodegradation. Among all the synthetic surfactants, non-ionic surfactants have garnered a great deal of attention in SESW studies [19, 62-66, 75, 81-82, 85-87, 122] because of their decreased adsorption characteristic in comparison to ionic surfactants, a decreased concentration requirement, a higher solubilization capacity, and increased performance [15, 81]. An intrinsic factor affecting the adsorption of non-ionic surfactants on soils is the alkyl chain length. In general, the adsorption of non-ionic surfactants increases with increasing alkyl chain length [122]. In addition to low adsorption characteristics, the environmental impact (toxicity) and retention of time

(biodegradability) of non-ionic surfactants should also be taken into considerations in selecting surfactants for use in SESW processes. Nonionic surfactants generally have high biodegradability [15, 63, 81], and low toxicity to soil microorganisms [63]. Rapid degradation of non-ionic surfactants in soil also aids to eliminate any adverse impact to the environment, because the more rapidly a material degrades, the lower the persistence or any long term adverse effects. However, studies on surfactant toxicity are limited. Grasso *et al* [61] stated that certain surfactants can be toxic to microorgranisms when present at levels above the critical micelle concentration.

1.2.2.2.2. Concentration selection

Concentration studies define the CMC value [82], as well as the minimum concentration for efficient washing [127]. Efficient surfactant solubilization of PAHs commences at the CMC and the solubility increases with increased concentration above the CMC value. Although certain researchers have operated with a surfactant concentration at the CMC level, this concentration was not efficient for PAHs removal. Chu *et al* [63] studied the mechanism of the SESW system and observed that the soil washing performance curve for selected HOCs increased exponentially with the increasing surfactant concentration. The same research group stated: "significant solubilization does not commence until a surfactant concentration is reached that is approximately two orders of magnitude greater than its CMC value" [16]. Zhou *et al* [127] also demonstrated that for an efficient removal of PAHs, much higher surfactant dosage was needed than CMC. However, high surfactant usage incurs a higher cost. To balance washing performance and cost, surfactant concentration needs to be carefully optimized.

1.2.2.2.3. Additional solubilization aids in the SESW system

In the surfactant-assisted soil washing system, additional aids are sometimes necessary to enhance either the desorption process or the partitioning process, depending mainly on the properties of the target PAHs and the soil matrix. Ultrasonication is the most common and inexpensive high energy source employed to enhance the performance of soil washing [123]. Ultrasonic energy is provided to break soil aggregates [123], to disrupt the electrostatic interactions between soil surfaces and PAHs, and perhaps even to also break certain very weak covalent bonds. Sonication has been demonstrated to be especially useful in soil washing when: 1) soil texture is fine-sized [123]; 2) SOM content is high [111]; and 3) PAHs are trapped within the three-dimensional structure of SOM [19]. Fine-textured soils contain higher proportions of silt, and clay, which are prone to form larger soil aggregates mediated by organic matter [123]. As a result, a considerable proportion of SOM is trapped into the soil macro-aggregates. Aggregation is followed by PAHs migration/internalization through partitioning processes. Without breaking the soil aggregates, both PAHs and SOM located at the inner surfaces of aggregates do not contact the surfactant micelle solution. Conte *et al* [123] compared the results between sonication and Soxhlet extraction and reported that sonication increased PAHs removal efficiency by 35% from a fine-texture soil. With the increase of SOM content, the size of aggregates increases accordingly and the SOM phase becomes more complex, which implies that PAHs are more deeply trapped within the cores of aggregates. The physical barriers that prevent contact with the aqueous phase are increased. That explains why sonication functions well during soil washing process

for each of the three cases: fine-texture soil, high SOM content and deeply trapped PAHs.

In addition to sonication, a buffer can be added into washing solution to maintain pH during the washing process [111]. The pH can have an appreciable influence on SOM desorption (as discussed previously), as well as on surfactant adsorption. The adsorption of surfactant decreased with increasing solution pH [122]. So, by maintaining an optimum pH, surfactant adsorption can be minimized and simultaneously, desorption of SOM can be increased. Ehsan *et al* [111] reported that by using a buffer and maintaining the solution pH at 8, PAHs removal efficiency was improved by 9%.

1.2.2.3. Research trends in SESW technology

Instead of optimizing the physical chemistry of the extracting solution to maximize desorption of PAHs, Ehsan *et al* [111] initiated a new washing system in which the properties of the geosorbent (soil) itself were altered to facilitate the mass transfer of PAH compounds from the soil matrix into the aqueous solution. The washing system was a mixed solution containing a non-ionic surfactant and a chelating reagent. The latter was aimed to loosen and scatter the SOM phase, so that the mass transfer of PAHs from soil inner phase into aqueous solution was facilitated. Yang *et al* [25] found that SOM, consisting mainly of FA and HA, were observed to be bound to inorganic minerals by polyvalent metal ion bridges (Fe^{3+}, Al^{3+}, Ca^{2+}, Mg^{2+}, etc.). These polyvalent metal ions also served as "cross-linking agents within the organic phase by binding to carboxylate or phenolate groups from different strands

of the humic macromolecules". As a result, the PAH partitioning process from inner soil matrix into aqueous phase was, therefore, impeded/blocked by the increased rigidity of metal-SOM networks. By complexing and removing of the metal ions, the networks were dissociated or at least the degree of cross-linking in soil organic matter phase was decreased. The resulting disaggregation facilitated the mass transfer of PAH compounds into aqueous solution and resulted in increased removal of PAHs [25]. The technique showed promising aspects in remediating field-contaminated soils in which PAH compounds have been incorporated into the soil inner matrix due to the aging process [111]. In the presence of chelating reagents, the removal efficiency of PAHs proved to be significantly greater (by 12% of chry and 16% of B[a]P) than control extractions in the absence of complexing reagent [111]. Although the washing conditions were not optimized and literature reports on this technique are limited, it suggests a technique to improve PAHs mobilization/removal efficiency.

1.2.2.4. Advantages of soil washing compared to in situ soil flushing

Soil washing is an ex situ soil remediation technology, and has been drawing great attention because of its advantages over in situ soil flushing [15, 19, 61, 80, 111].

1) it represents a permanent and inexpensive solution;
2) it is conducted in a closed system, and so the conditions can be optimized and well controlled;
3) it can avoid pollutants, surfactants, or/and additives downward migration into water tables as in situ flushing does;
4) it is efficient, fast and complete;

5) less surfactants or additives remaining in soils after treatments;
6) it can remove organic pollutants as well as inorganic pollutants at the same time;
7) public acceptance is high.

1.3. Objectives of the study

1.3.1. Overall objective

Optimize a soil washing procedure consisting of the combination of surfactant, chelating reagent, and ultrasonic energy to cleanup soils that have been heavily contaminated with PAH compounds over a long period of time, so that following the treatment, the cleaned soil would meet the federal legislative norm promulgated by the Canadian Council of Ministers of the Environment (0.6 μg g^{-1} soil for B[a]P and 2.1 μg g-^{1} soil for chrysene) [128].

1.3.2. Specific objectives

1) Determine the effective concentration of selected surfactant

Based on previous studies on surfactant screening [19, 111], a non-ionic surfactant, Brij98, was chosen for use in this project. The CMC of Brij98 was tested as 3% (V/V) during previous work. In the current study, four concentrations, 0.5 × CMC, 1 × CMC, 1.5 × CMC, and 2 × CMC, will be investigated and compared.

2) Investigate the influence caused by the addition EDDS into surfactant solution

The PAH removal efficiency caused by the addition of EDDS in surfactant solution will be compared with control solution (surfactant alone). Two of the most toxic PAH compounds, four-ringed chrysene (chry) and five-ringed B[a]P, are the targeted compounds.

3) Optimize the operational variables in surfactant-chelating reagent mixed system

The operational variables include:

1) Brij98 and EDDS concentrations;
2) Solution pH;
3) Ultrasonication time;
4) Solution/soil ratio;
5) Metal-cleanup in recovery solution;
6) Sequential washing cycles.

4) Evaluate the optimized soil washing procedure

1.4. Hypothesis

Based on the discussions earlier, it can be seen that, theoretically, a mixed surfactant system seems to be the better choices for remediating PAHs contaminated soils [75, 122]. However, a surfactant system alone does not solve the problems caused by metal ion cross-linking within SOM phase. So, in our experimental design, instead of using a second surfactant for a mixed system, a chelating reagent was chosen to be incorporated into a non-ionic surfactant to solve a major problem present in the soil. The soil has very high organic matter content (~60%), and has been historically

contaminated with PAHs during 100 years. Theoretically, the majority of PAHs, especially the two most hydrophobic PAHs chrysene and B[a]P, have fused into the organic matter fraction and perhaps formed strong chemical bonds with humic acids due to the profound and long aging process. In order to release PAHs entrapped inside the organic fraction, the metal bridges linking HA molecules have to be broken and removed from the organic fraction to open the pathway for PAH molecules to partition into the surfactant micelles of the aqueous phase. Our hypothesis was that by using the surfactant-chelating system, the solubility of PAHs can be greatly enhanced in comparison to a single surfactant system, or a mixed surfactant system. A single surfactant alone does not have the ability to break the metal linkages among the HA networks and consequently has little solubilizing power for PAH compounds trapped within the soil matrix – HA networks. In addition to the enhancement of PAHs solubility, the selected system might also enhance the removal of inorganic contaminants – heavy metals.

A multi-step sequential washing, as a cost effective component of a soil washing system, has been investigated in previous studies [19, 111]. The efficiencies of fresh solution *vs.* recovery solution at each washing step were studied and the results demonstrated that there were no appreciable differences between fresh and recovered solutions in terms of PAHs removal [111]. The reason was probably that although recovery solution had a smaller amount of surfactant compared to fresh solution, the DOM made up for the lost micelle capacity in the recovered solution. The detergency and complexing property of DOM (*i.e.* HA and FA) have been well established [47, 49, 123-126, 129]; so the DOM functions as both surfactant and chelating

reagent in recovery solution. In this soil washing study, instead of using fresh solution for each washing cycle, the recovered solution will be used following the first washing. By saving the sequential washing solutions, the cost of processing might be decreased.

Chapter 2. Materials and Methods

2.1. Chemicals

[*S,S*] Ethylenediaminedisuccinic acid, [*S,S*]-EDDS, 30% W/W), Octaquest E30, was purchased from Innospec Limited, Cheshire, UK. B[a]P, chrysene and Brij98, a non-ionic surfactant, were obtained from Sigma-Aldrich Co., Oakville, ON, Canada. Methyl isobutyl ketone, MIBK, hexane, and ethanol were purchased from Fisher Scientific, Napean, ON, Canada. Standard solutions (Al, As, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Zn), 1000mg l^{-1}, for ICP determinations were obtained from Sigma-Aldrich, Co., Oakville, ON. All chemicals, solvents, and reagents were of ACS Reagent grade or better.

2.2. Soil sampling and Characterization

The soil used in this study was obtained from a tar pond site in Sydney, Nova Scotia, Canada. The soil had been heavily contaminated with PAH compounds during a century's accumulation of steel production effluents. The sample was air-dried, passed through 2 mm sieve and stored in a tightly sealed plastic container.

The soil was characterized with respect to particle size, pH, cation exchange capacity (CEC), organic matter, and heavy metal content. The particle size (% sand, silt, and clay) was determined by the Bouyoucos' method (1962) [130] and CEC was determined with the Rhoades procedure [131]. The pH was determined in soil slurry (soil to water ratio of 1: 2.5) with a combination electrode using a CORNING model 220 pH meter. The determination of organic matter followed the procedure of the

America Society for Testing and Materials (ASTM, 1993) [132]. The contents of heavy metals were determined with inductively coupled plasma – atomic emission spectrometry (ICP-AES) in clear solutions that resulted from block digestion using nitric acid plus hydrogen peroxide. The total burdens of the two selected PAH compounds, chrysene and benzo[a]pyrene (B[a]P), were determined by exhaustive Soxhlet extraction [111].

2.3. Soil washing

The soil washing procedures for all the trials were similar, with only slight differences in terms of the concentration of surfactant/chelating reagent in the mobilizing solution, solution pH and volume, soil mass, ultra-sonication time, and with/without metal clean-up in the recovery solutions. In general, soil was added into 50 ml plastic centrifuge tubes and equilibrated with mobilizing solution in the presence of ultrasonic energy provided by an ultrasonic homogenizer (XL 2020 Sonic dismembrator, Misonix Inc. NY). An extended horn of 25 cm (L) x 1.2 cm (W), tuned at 20 kHz frequency, delivered ultrasonic energy (240 W) in a pulsed mode with a fixed vibration amplitude setting of 7. Sonication was performed with tubes at room temperature while the attendant heating increased the temperature to ~60^{o}C. The equilibration consisted of pulsed surges of power delivered for 2 s followed by a 2 s cooling phase. Post sonication, the resulting suspensions were centrifuged at 5000 rpm for 1 h with IEC Multi-RF Refrigerated Centrifuge (ThermoIEC Inc. US). Then the solid soil phase was either equilibrated again with recovery solution or subjected to further treatments (block-digestion or sequential

extraction for metal analysis). The supernatant fraction was back-extracted with a mixture of solvents, hexane-MIBK (9:1), for the subsequent GC/MS analysis.

2.4. Back-extraction

The back-extraction step transferred PAH compounds from the soil extract (supernatant fraction) to the hexane-MIBK phase. The PAHs contained in the hexane-MIBK mixture were analyzed by GC-MS and the aqueous fraction, post removal of PAH compounds, was assayed either to determine the metal content that had been mobilized by the complexing reagent (EDDS or EDTA) or was reused for subsequent washing cycles depending on the experimental design.

The back-extraction procedure was performed as follows. The soil supernatant fraction was equilibrated three times sequentially with 5 ml of hexane-MIBK mixture (9:1) to partition PAHs from the soil washes. The three hexane-MIBK fractions were combined (in a 20 ml glass tube) and amended with 1 ml of ethanol to break the emulsion induced by agitation. Finally the glass tube was tightly sealed and the hexane fraction was vigorously agitated to obtain a clear solution. Then the hexane solution was concentrated to 1 ml under a gentle stream of N_2. The concentrated hexane was transferred into a 2 ml vial, which was stored in a refrigerator to await GC-MS analysis.

The soil supernatant fraction, after removal of PAHs, was either added back to the original centrifuge tube containing the soil particulates fraction for the next

equilibration or centrifuged again at 5000 rpm to remove fine particles that otherwise might block the ICP-AES delivery system during metal content analysis.

2.5. GC/MS analysis

GC-MS determinations were performed with a Varian model 3900 gas chromatograph equipped with a model 8400 autosampler and a model 2100T MS detector. The chromatographic separation of PAHs was performed on a 30 m × 0.25 mm i.d. and 0.25 μm film thickness of DB-5 capillary column (Varian Inc., Palto Alto, CA, USA). Helium, at 1.0 ml min^{-1}, served as the carrier gas. The GC oven temperature was programmed as follows: the initial temperature was set at 100°C with no hold time, and the column was ramped at 3°C min^{-1} to 233°C, then the ramp rate was decreased to 0.1°C min^{-1} until the temperature reached 234°C. Subsequently, the temperature was ramped at 3.0°C min^{-1} to 251°C, and then further reduced to 0.2°C min^{-1} until 252°C with a further hold time of 5 min prior to cool down. The temperature of the injector was maintained at 260°C and injections were performed in the splitless mode. The transfer line, trap, and manifold were maintained at 250°C, 150°C, and 100°C respectively. Identification of the eluting compound was performed by comparing the experimental mass spectrum with the spectrum of the standard as well as the spectrum catalogued in the National Institute of Standards and Technology (NIST) or the Saturn mass spectral libraries.

2.6. Soxhlet Extraction

Soil, 1 g, was transferred to a cellulose thimble and extracted with 150 ml of hexane-acetone mixture (3:1) for 24 h at a rate of 10 to 12 cycles per hour. For the determination of the initial PAH burdens, the extract was concentrated to 3 ml by a rotary evaporation, and then transferred into a 25 ml of volumetric flask with hexane-MIBK mixture (9:1). As to the analysis of remaining PAH residues in the soil particulates fraction after nine sequential washes, the extract was concentrated to 1 ml under a gentle stream of N_2. The resulting solutions were placed in a refrigerator and await for GC/MS analysis.

2.7. Block digestion

Solutions for determinations of the total metal burden were prepared by **Block-Digestions** using the conventional method established by Sommers and Nelson, 1972 [133] with only minor modifications. A mixture of nitric acid and hydrogen peroxide were used instead of nitric/perchloric acid to circumvent the possible explosive character of perchlorate salts and the soil weight taken for analysis was decreased to 0.16 g due to the high organic matter content (59%) in the soil. Prior to ICP analysis, the digested solutions were sonicated in an ultrasonic bath for 1 h (to dissolve any solid that adhered to the inner surfaces of the digestion tube) then diluted to 15 ml with distilled deionized water (DDW). The clear supernatant fractions that resulted from centrifugation for 30 min were analyzed for total metal burdens by ICP-AES.

2.8. Sequential extraction

Sequential extractions were performed according to the BCR three-step sequential extraction procedure [134] with minor modifications to determine metal distributions in various soil fractions. In short, 0.10 g soil or soil residue was extracted sequentially with solution A (11 ml) then solution B (11 ml) in a 15 ml of centrifuge tube for 24 hours with a mechanical, end-over-end rotary shaker at a speed of 30 rpm. Solution A (acetic acid, 0.11 mol l^{-1}) and B ([hydroxylammonium chloride, 0.5 mol l^{-1}) were modified with Brij98 (3 ml of 3% Brij98 in 100 ml solution), which served as wetting agent for the sample soil containing a high content of organic matter. The last step of the extraction sequence involved in a series of low temperature digestions with 30% (V/V) hydrogen peroxide (acid-stabilised to pH 2–3). The series of low temperature digestions was performed as follows: soil residue**,** from step 1 and step 2 extractions**,** was digested in a centrifuge tube with 2 ml of 30% hydrogen peroxide at room temperature overnight. The temperature was maintained at 40°C for 3 hours in a water bath then increased to 85°C and held for 4 hours and lastly the solution was heated at 60°C to reduce the volume to ~0.5 ml. Subsequently, 2 ml of 30% (V/V) hydrogen peroxide was added and the digestion sequence described above was repeated. After cooling, 13 ml of solution D (ammonium acetate, 1.0 mol l^{-1}) was added into the digestion tube and the contents were sonicated in an ultrasonic bath for 1 h to dissolve any solid that adhered to the inner wall of the digestion tube. Finally**,** the solution that resulted from each extraction step was centrifuged and the supernatant was analyzed by ICP-AES for metals content.

2.9. ICP analysis

The metal contents of Al, As, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, and Zn were analyzed by ICP-AES, model VISTA-MAX (Varian Australia Pty Ltd., Australia). Along with the soil samples, a standard reference material (SRM) — "Montana Soil 2710" was used to evaluate the ICP results. Multiple emission lines for each element were selected to assess spectral interferences and a FACT (Fast automated correction technique) model was used to correct for possible interferences.

2.10. Chelating reagent selection

Two series of trials were completed in this phase of the study. One trail was aimed at evaluating the influence of chelating reagents on the enhancement of PAH removal and involved a series of equilibrations of soil with an aqueous surfactant solution in the presence/absence of test chelating reagent. The other trial was conducted to compare the PAH mobilization efficiency of EDDS with that of EDTA in surfactant-based solution. All of the equilibrations of soil with mobilizing solutions were conducted following the soil washing procedure described previously.

2.10.1. Chelating reagent enhancement study

Soil, 3 g, was added to a 50 ml centrifuge tube containing 30 ml of 6% (V/V) Brij98 in the presence/absence of 0.1M EDDS. The original pH of the mobilizing solution with the addition of EDDS was 9.0, so the control solution (pure Brij98, without EDDS) was adjusted to the same pH. After the first equilibration which was performed with the fresh washing solution, four sequential equilibrations were

conducted using the solution recovered from the previous washing trial (five equilibrations in total). During each equilibration, ultrasonic energy was applied for 30 min, and pH values were measured post each equilibration. The resulting suspension was centrifuged at 5000 rpm for 1 h, and the supernatant subjected to back-extraction and subsequent GC/MS analysis. Post the first soil wash with fresh solution, the soil particulates fraction was equilibrated with the same 30 ml of mobilizing solution that had been recovered from the previous wash. The soil residuals after five sequential washing cycles were oven-dried at 60°C and measured for organic matter loss (by weight). The soil particulates fractions, then, were subjected to further treatment – block-digestion and sequential extraction (as described previously). The resulting solutions were centrifuged and the supernatants were analyzed for metals content by ICP-AES.

2.10.2. Chelating reagent selection study

Soil, 2.5 g, was equilibrated with 25 ml of mobilizing solution in a 50 ml centrifuge tube during 10 min under ultrasonication. The variable in this trial was the chelating reagent (0.05 M EDDS *vs*. 0.05 M EDTA) and each of the chelating reagent solutions was adjusted to either of two pH values (6.0 or 9.0). Each solution was formulated to contain 3% (V/V) Brij98. Post equilibration, the suspensions were centrifuged, and then the pH values of the supernatant fraction was measured. Afterwards, the supernatants were back-extracted to transfer PAH compounds to a hexane phase, which was concentrated to 1 ml under a gentle stream of N_2. The concentrated hexane was transferred to a 2 ml vial and analyzed by GC/MS.

2.11. Effect of pH

The quantities of mobilized PAHs, as influenced by pH, were systematically evaluated in this trial. The mobilizing solution (6% Brij 98 (V/V) + 0.10 M EDDS) was adjusted to one of 6 pH levels (5.0, 6.0, 7.0, 8.0, 9.0 or 10.0). Soil washing, back-extraction, and GC/MS analysis were conducted according to the procedures described above. In addition, a parallel trial without ultrasonication was conducted to assess the influence of ultrasound on PAH recovery. In this trial, 3 g of soil was equilibrated with 30 ml of mobilizing solution for more than two months without ultrasonication. All the other conditions remained the same including soil mass, solution composition, pH and volume, back-extraction procedure, and GC/MS conditions.

2.12. Effect of ultrasonication time

The mobilizing solution for the ultrasonication time trial was 6% (V/V) Brij 98 formulated in 0.10 M [*S,S*]-EDDS. There were five ultrasonication times, 5, 10, 15, 20 or 30 min. The soil washing procedure remained unchanged from previous trials. In brief, soil, 3 g, in a 50 ml centrifuge tube, was mixed with 15 ml mobilizing solution, and sonicated for 5, 10, 15, 20 or 30 min. The equilibration consisted of pulsed surges of power delivered for 2s followed by a 2s cooling phase using the ultrasonic homogenizer. The resulting suspension was centrifuged then back-extracted with hexane-MIBK as outlined above to recover PAH compounds from the aqueous supernatant fraction. The resulting hexane fraction was concentrated and then determined for PAHs by GC/MS.

2.13. Surfactant and EDDS concentration selection

Two independent trials were conducted in this phase of studies. Four levels of Brij98 concentration (1.5%, 3%, 4.5%, and 6%) and three levels of EDDS concentration (0.05 M, 0.10 M, and 0.15 M) were evaluated for efficiency of PAH mobilization. The control solution for Brij98 concentration trial contained 0.05 M EDDS, and the control solution for the EDDS concentration trial contained 3% (V/V) Brij98. The solution pHs of both trials were ~9 (original pH without adjustment). Soil**,** 2 g**,** was equilibrated with 20 ml of mobilizing solution, then back-extracted with 15 ml of hexane-MIKB (9:1) mixture and the organic phase was concentrated to 1 ml followed the procedures described previously. The resulting solutions were analyzed by GC/MS for B[a]P.

2.14. Metal clean-up trial

Following the same general procedures, 3 g of soil was washed with 30 ml mobilizing solution containing 6% (V/V) Brij98 plus 0.10 M EDDS (pH 9). After back-extraction, metal ions in the supernatant fraction were removed by reaction with Mg^0 flakes. There were 3 levels of Mg^0 additions to the ~27 ml recovery solutions: 0.053 g, 0.073 g, and 0.144 g, which corresponded to molar ratio of Mg^0/EDDS 0.73, 1.00, and 2.00. Prior to Mg^0 reaction, the pH of each of the recovery solutions was adjusted to 4.0 in order to solubilize the coatings on Mg^0 flakes; otherwise the reactions were very slow. The vigorous reactions lasted up to 1 h. Subsequently, the solutions were centrifuged and pH values were measured in the supernatant fractions. Prior to the next washing cycle, the solution pHs were all adjusted to approximately the same pH value (~9). Following the first equilibration

which was conducted with fresh washing solution, three more washing cycles were completed using the recovery solutions with metal ions being removed by reaction with Mg^0 flakes. Each of the hexane fractions resulted from back-extraction was analyzed for PAH content. The soil residues post four washing cycles were block-digested and analyzed for metals content. The content of metals was compared with extractions of the control that did not have any addition of Mg^0 flakes.

2.15. Solution/soil ratio trial

Two solution/soil ratios were evaluated; 3.3 and 6.6. In particular, 3 g or 6 g of soil was equilibrated with 20 ml of mobilizing solution containing 6% (V/V) Brij98 and 0.10 M EDDS. The soil washing procedure and subsequent analyses were similar to the previous sections.

2.16. Procedure test

Based on the results from the trials described above, the optimized operating variables were identified and evaluated. Nine soil washing cycles were performed following the parameters summarized below and (the soil washing procedure and analyses remained the same). All trials conducted in this project were performed in triplicate.

Optimized operatng variables:

1) Chelating reagent concentration:	0.10 M EDDS
2) Surfactant concentration:	6% (V/V) Brij98
3) solution pH:	9.0

4) Ultrasonication time: 30 min.

5) Solution to soil ratio: 6.6:1 (V/W)

6) Recoveries were performed in the absence of a metal precipitation sequence.

3. Results and Discussion

3.1. Characteristics of the soil

The relevant physical and chemical properties of the soil sample as well as the total burden of chrysene and B[a]P are summarized in Table 3-1.

Table 3-1. The characteristics of the soil sample.

Sand (%)	Clay (%)	Silt (%)	Organic C (%)	pH	CEC (cmol kg^{-1})	Chrysene ($\mu g\ g^{-1}$ soil)	B[a]P ($\mu g\ g^{-1}$ soil)
47	8	45	59	3.5	23	215	234

The soil was classified as a sandy loam according to the US Department of Agriculture classification system (USDA Texture triangle). The extremely high contents of both organic matter and PAH compounds, low pH, and intermediate CEC suggested that to clean-up the PAH contamination by soil washing might be challenging. The total burdens of the two selected PAH compounds, chrysene and benzo[a]pyrene (B[a]P), were determined after exhaustive Soxhlet extraction [111] and the total metal burdens (Table 3-2) were determined by ICP-AES in clear solutions prepared by conventional nitric acid block-digestions with minor modifications (hydrogen peroxide was used instead of nitric/perchloric acid to circumvent the possible explosive character of perchlorate salts and the soil weight taken for analysis was decreased to 0.16 g due to the high organic matter content (59%) in the soil). Standard Reference Material (SRM) **Montana Soil 2710**, from the National Institute of Standards and Technology (NIST), was included for quality control purposes. The results of quality control sample were in good agreement with

the certified values for the analyte metals. Among all the contaminants tested, B[a]P, chrysene, and all of the heavy metals were highly elevated and were in excess of the

Table 3-2. Toxicant burdens and permitted maxima.

Toxicant	Total content		CCME[a] Guideline ($\mu g\ g^{-1}$ soil)			
	($\mu g\ g^{-1}$ soil±1SD)	($\mu mol\ g^{-1}$ soil±1RSD)	Agr[b]	Residential / Parkland	Ind[c]	Comm[d]
B[a]P*	234±27		0.6	0.6	0.6	0.6
Chry*	215±22		2.1	2.1	2.1	2.1
Al	14250±860	528±6%				
As**	355±28	5±8%	12	12	12	12
Cd**	39±3.0	0.35±8%	1.4	10	22	22
Cr**	135±12	2.6±9%	64	64	87	87
Cu**	560±36	9±6%	63	63	91	91
Fe	170000±1050	3044±0.6%				
Mn	2000±165;	36±8%				
Ni**	55 ±2.7	0.9±5%	50	50	50	50
Pb**	630±46	3±5%	70	140	600	260
Zn**	390±22	6±6%	200	200	360	360
	$\Sigma_{HMs} \cong 3.6$ mmol g^{-1} soil		EDDS charge, 2.0 mmol, 0.18 x Σ_{HMs}			

[a.] Canadian Council of Ministers of the Environment (CCME) [128]. [b] permissible residues in soil destined for agricultural use; [c] permissible residues in soil destined for industrial use; [d] permissible residues in soil destined for commercial use.

* CCME guidelines, 2008 [128].

** CCME guidelines, 2007 [135].

Canadian Council of Ministers of the Environment (CCME) guidelines for agricultural, residential/parkland, commercial or industrial use. So, based on the contaminant levels, both PAH compounds and heavy metals became targeted contaminants to be addressed in soil washing studies.

3.2. Chelating reagent selection

The selection of a suitable chelating reagent involved two studies. The first trial investigated the effects of a chelating reagent (0.1 M EDDS) on the enhancement of PAHs removal as well as the influences on metal remediation with an aqueous surfactant- {6% (V/V) Brij98} based mobilizing solution. The original solution pHs were the same (pH approximately 9). This trial involved five sequential washings. Following the first equilibration which was performed with fresh mobilizing solution, four sequential washes were conducted using solution recovered from the original 30 ml of mobilizing solution and the pH value was measured after each equilibration. The metal contents in soil residues as well as in each fraction of the soil residues post five washings were also determined. Organic matter loss was calculated by subtracting the total weight of all metals from the total soil weight loss after the five soil washings.

The second trial compared the efficiencies of EDDS with that of EDTA on PAH mobilization into aqueous surfactant solutions. The solutions contained 0.05 M EDDS or EDTA and 3% (V/V) Brij98, and each solution was adjusted to either of two pH values (6 or 9) before equilibrations with the soil. During equilibrations,

ultrasonic energy was supplied as described in **Materials and Methods** section, and the trials were all conducted in triplicate.

3.2. 1. EDDS enhancement on PAH removal

The enhancement by EDDS on PAHs removal is presented in Table 3-3. The presence of EDDS increased B[a]P mobilization by 15% in total during five successive soil washings; after this stage, 93% of total B[a]P was removed from the soil. The increased removal for B[a]P by EDDS remained fairly high throughout all the five washing cycles (15% - 32%). The first washing was the most efficient one, which removed 32% of the total B[a]P from the soil; the second removed less than 25%, and the third even less, and so on.

Table 3-3. The EDDS **e**nhancement on B[a]P and chrysene removal (μg g^{-1} soil).

	Treatment	1^{st} washing (μg g^{-1} soil ± 1SD)	2^{nd} washing (μg g^{-1} soil ± 1SD)	3^{rd} washing (μg g^{-1} soil ± 1SD)	4^{th} washing (μg g^{-1} soil ± 1SD)	5^{th} washing (μg g^{-1} soil ± 1SD)	Total removed by 5 washings
B[a]P	Surfactant alone	64 ± 4	49 ± 4	34 ± 8	20 ±2	15 ±1	78%
	Surfactant+EDDS	76 ± 5	57 ± 6	42 ± 5	24 ± 1	20 ±1	93%
	% increase by EDDS	16	14	19	17	25	15%
Chrysene	Surfactant alone	92 ± 4	56 ± 3	32 ±1	18 ± 1	3 ± 0.2	93%
	Surfactant+EDDS	99 ± 4	57 ± 2	33 ± 5	16 ± 1	4 ± 0.4	97%
	% increase by EDDS	7	2	3	– 12	25	4%

In contrast to B[a]P removal, the influence of EDDS on chrysene mobilization was not as pronounced; although the removal rate by EDDS was slightly higher than

control (4% of more chrysene was removed by EDDS after five washings). However, chrysene was more readily mobilized into the mobilizing solutions in comparison to B[a]P. Even without EDDS addition, chrysene removal reached 93% after 5 washes. The different behaviours of EDDS on the mobilization of chrysene or B[a]P indicated that chrysene and B[a]P in the soil possessed different geochemical properties: 1) chrysene might not have been bound to the soil organic fraction through metal linkages or at least the degree of metal links might have been much less in comparison to B[a]P; and 2) chrysene might have been located mainly on the outer surfaces of organic matter fraction, which provided an easier access to mobilizing solution or 3) the solubility of chrysene is greater than the solubility of B[a]P.

Table 3-4 presents the pH variations during the five soil washings. Two mobilizing solutions, with/without EDDS addition, had the same original pH values (9.15). Interestingly, the pHs of control solutions decreased sharply from 9.15 to 3.76 after

Table 3-4. Variations in pH values post each soil equilibration.

Mobilizing Solution	Original pH	Post 1st washing	Post 2nd washing	Post 3rd washing	Post 4th washing	Post 5th washing
6% (V/V) Brij98 alone	9.15 ±0.00	3.76 ±0.01	3.81 ±0.02	3.85 ±0.01	3.88 ±0.02	3.95 ±0.03
6% (V/V) Brij98+ 0.1M EDDS	9.15 ±0.00	8.54 +0.01	8.56 ±0.01	8.59 ±0.02	8.62 ±0.03	8.67 ±0.03

the first equilibration, and remained almost constant with only slight increases post each successive washing; whereas the pHs of the solutions with EDDS addition

remained distinctly alkaline range (pH, 8.54), and also remained almost constant with only sight increases during the subsequent equilibrations. Apparently, the mobilizing solution with surfactant alone (SF) had little buffering capacity, so that the soil slurry had little resistant to pH changes (soil pH was 3.5); whereas the mobilizing solution that contained EDDS (SE) possessed a much greater resistance to pH changes. The increased buffering capacity of EDDS might have been the key factor which was responsible for the increased B[a]P removal.

The amount of dissolved organic matter (DOM) in washing solutions has always been closely associated with the removal rates of PAHs. Generally, the more DOM in solution, the higher the PAH mobilization rate of the soil washing procedure [25-28, 31, 37, 39]. The total losses of organic matter (OM) by different washing solutions after five successive equilibrations are indicated in Figure 3-1. The total loss of OM in the presence of EDDS reached 48% of the total OM in soil, whereas the loss of OM to the control solution was 33%, which amounted to 15% less OM dissolution. Interestingly, the difference of OM loss between the two mobilizing solutions (EDDS addition *vs.* control) matched well with the enhanced B[a]P removal rate (15%) by EDDS. Although it might have been a coincidence, a relationship between the two parameters is implied. It is not difficult to rationalize that the percentage of organic matter lost to mobilizing solution could be the same percentage as B[a]P gained by the solution. After all, B[a]P mobilization has been considered as an accompanying process of organic matter dissolution when B[a]P is deeply fused into the inner surfaces of the soil organic fraction [25,].

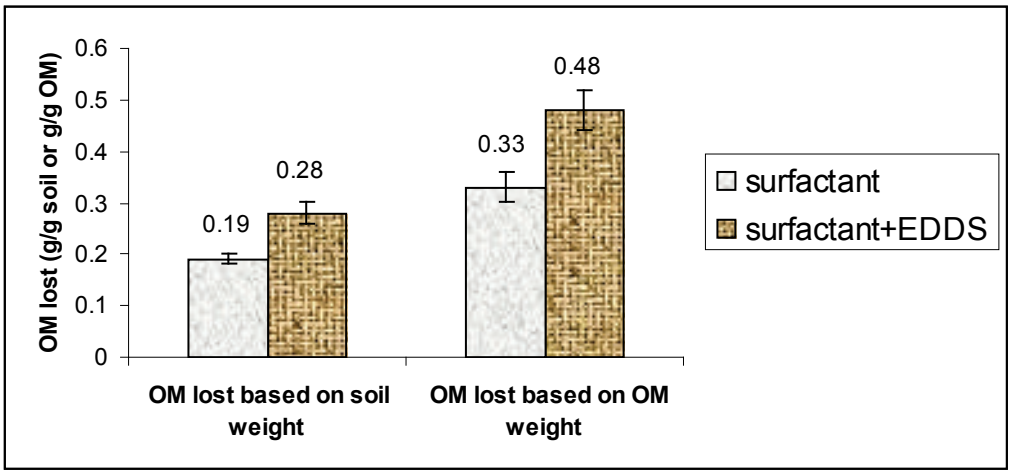


Figure3-1. Organic matter loss during five successive soil washings.

In addition to the measured data, the color of the suspension or the supernatant fraction after equilibration can also serve as an indicator of soil washing efficiency [25]. The difference in color intensity or darkness between EDDS and control extracts in Figure 3-2 provided a direct visual comparison of OM dissolution. The color of

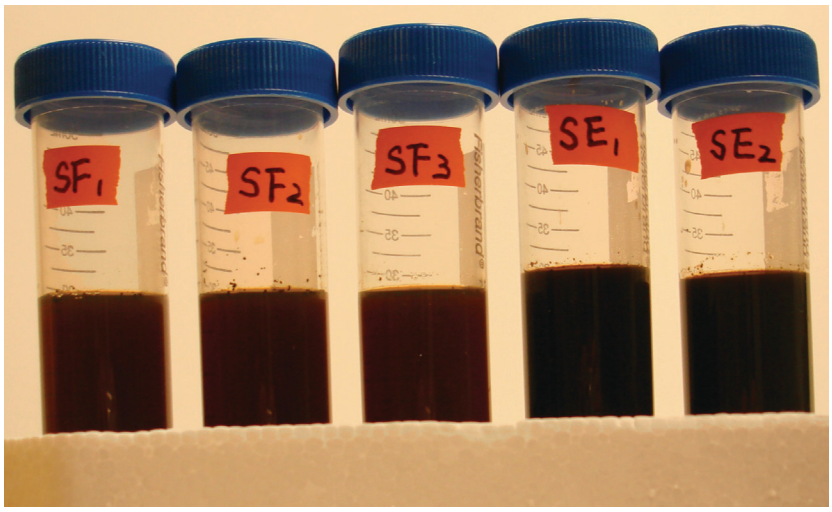


Figure 3-2. The color difference between extracts of EDDS and control.

the control extracts (SF) was reddish brown; whereas that of EDDS extracts (SE) became much darker or near black suggesting that more OM was dissolved into the aqueous solutions.

The determination of metals that remained with each fraction of soil particulates might provide a greater insight into the soil washing process. The metals removed from the various soil fractions are presented in Table 3-5. The total quantity of each metal removed from the soil profile represented the increased mobilization efficiency induced by EDDS. The total amount of each metal removed from the soil in the presence of EDDS was appreciably greater than that by surfactant alone. Cd removed by EDDS was 18 fold greater than that by control (surfactant alone), followed by Cr, Fe, Al, Cu, Pb, As, Ni, and Zn which were 15 fold, 4.7 fold, 4.4 fold, 4 fold, 1.3 fold, 64%, 54%, and 35% respectively greater by EDDS than by control. Ca was the last metal which had an increased percentage (17%) by EDDS in comparison with control. As to Mn and Mg, EDDS showed no positive effect on their extraction, because the increased percentages for Mn and Mg were negative (–12% and –21% respectively).

While the total quantities of metals removed from the whole soil profile represent the metal remediation powers of EDDS, the metals associated with organic fraction of the soil provide some insights into the PAH remediation process. Among the twelve metals analyzed, eleven metals (except Ca) had a similar distribution pattern among the four soil fractions (exchangeable, reducible, oxidizible, and residual). The organic fraction contained the highest amount of metals and ranged from 42% to 85% except Ca, which had the highest percent (60%) within exchangeable fraction. This distribution pattern applied to both the original soil and the soil particulates fraction after five washings. The distribution pattern of the metals implied that the remediation of heavy metals would be difficult in the absence of a

Table 3-5. Metals (μg g^{-1} soil ±1SD) left with each of the four fractions of the soil particulates post five soil washing cycles.

Metal	Soil fraction	Composition of the Original Soil		Residues Post SF	Residues post SE	Total removed by SF	Total removed by SE	Increased removal by EDDS
		(μg g^{-1} soil ±1SD)	%	(μg g^{-1} soil ±1SD)	(μg g^{-1} soil ±1SD)			
	Exchangeable	815±22	6	484±13	416±28			
Al	Reducible	1646±22	12	1587±98	452±30	579	3113	4.4-fold
	Oxidizible	6625±350	46	6436±44	5105±171			
	Residual	5164	36					
	Exchangeable	17±1	5	8±0.9	11±1			
As	Reducible	86±7	24	32±4	44±3	66	108	64%
	Oxidizible	250±12	70	247±21	190±20			
	Residual	2	1					
	Exchangeable	4749±199	60	1258±94	1249±83			
Ca	Reducible	460±64	6	249±14	71±8	3717	4361	17%
	Oxidizable	1330±134	17	1315±120	858±77			
	Residual	1341	17					
	Exchangeable	10±1	26	10±1	8±0.9			
Cd	Reducible	11±1	28	10±0.9	6±0.4	1.1	20.6	18-fold
	Oxidizable	17±1	43	17±2	4±0.5			
	Residual	1	2					
	Exchangeable	3±0.3	2	3±0.2	3±0.2			
Cr	Reducible	6±0.8	4	6±0.5	3±0.3	3	47	15 fold
	Oxidizable	100±3	74	97±7	56±3			
	Residual	26	19					
	Exchangeable	30±3	5	14±1	10±1			
Cu	Reducible	62±3	12	58±3	25±3	40	158	4-fold
	Oxidizable	350±34	62	330±28	249±21			
	Residual	118	21					
	Exchangeable	1816±26	1	119±6	1784±141			
Fe	Reducible	18241±305	11	17589±816	7770±491	3245	18528	4.7-fold
	Oxidizable	115627±3224	68	114731±3022	107602±3324			

	Residual	34316	20					
	Exchangeable	204±8	23	11±1	43±2			
Mg	Reducible	45±3	5	27±1	30±2	261	205	–21%
	Oxidizable	450±40	50	400±42	421±43			
	Residual	201	22					
	Exchangeable	114±9	5	8±0.8	17±1.7			
Mn	Reducible	38±2	2	33±3.2	29±2.9	151	133	–12%
	Oxidizable	1190±110	60	1150±100	1163±110			
	Residual	658	33					
	Exchangeable	4±0.4	7	1±0.2	0.1±0.06			
Ni	Reducible	5±0.4	9	0±0	2±0.2	9.6	14.8	54%
	Oxidizable	47±2.0	85	46±4.0	40±4.2			
	Residual	-1	-1					
	Exchangeable	75±5	12	41±3	6±0.7			
Pb	Reducible	192±15	30	182±5	127±13	156	355	127%
	Oxidizable	359±7	57	247±17	138±11			
	Residual	4	1					
	Exchangeable	148±15	38	17±1	2±0.2			
Zn	Reducible	43±4	12	26±2	26±2	159	215	35%
	Oxidizable	166±14	42	155±12	114±9			
	Residual	33	8					

suitable chelating reagent. The results in Tables 3-5 indicate that metals associated with the exchangeable fraction were much more readily extracted by control solution (surfactant alone) than from the organic fraction. The extraction efficiencies of the majority of metals, except Cr and Cd, by surfactant from the exchangeable fraction ranged from 41% to 95%; whereas extraction efficiencies from the organic fraction decreased to less than 5%. By adding EDDS into the extracting solution, the metal recoveries from the organic fraction increased considerably (Table 3-6). So, in

order to mobilize the heavy metals located within organic fraction, it was necessary to add a chelating reagent into the surfactant-based solution.

Table 3-6. EDDS enhanced removal of metals from the organic fraction.

Percent of metal removed (based on the total burden in **organic fraction**)					Quantity of metal removed from the **organic fraction**				
Order	Metal	By SF (%)	By SE (%)	Increased removal by EDDS (%)	Order	Metal	Removal by SF ($\mu g\ g^{-1}$ soil)	Removal by SE ($\mu g\ g^{-1}$ soil)	% based on the total metal removed by SE
1st	Cd	1	77	76	1st	Fe	896	8025	76
2nd	Cr	3	44	41	2nd	Al	189	1520	14
3rd	Ca	1	35	34	3rd	Ca	15	472	4
4th	Pb	31	62	31	4th	Pb	112	221	2
5th	Zn	7	31	24	5th	Cu	20	101	1
6th	Cu	6	29	23	6th	As	3	60	0.6
7th	As	1	24	23	7th	Zn	11	52	0.5
8th	Al	3	23	20	8th	Cr	3	44	0.4
9th	Ni	2	15	13	9th	Mg	50	29	0.3
10th	Fe	1	7	6	10th	Mn	40	27	0.3
11th	Mn	3	2	–1	11th	Cd	0.1	13.3	0.1
12th	Mg	11	6	–5	12th	Ni	1	7	0.1
The sum of metals removed by SF from the organic fraction = **1340 ($\mu g\ g^{-1}$ soil)** The sum of metals removed by SF in whole soil profile = **8388 ($\mu g\ g^{-1}$ soil)**					The sum of metals removed by SE in organic fraction = **10571 ($\mu g\ g^{-1}$ soil)** The sum of metals removed by SE in whole soil profile = **27258 ($\mu g\ g^{-1}$ soil)**				

In addition, metals in the soil residual fraction (Table 3-5) seemed to fall into one of the two distinct categories: either 1% - 8% (As, Cd, Ni, Pb, and Zn) or 17% - 36%

(Al, Ca, Cr, Cu, Fe, Mg, and Mn). Metals within the residual fraction are not available for remediation processes by complexometric extraction nor to micro-organisms or plants. Consequently, a relatively high proportion of Al, Ca, Cr, Cu, Fe, Mg, and Mn in the residual fraction would not be extracted by soil washing solutions nor cause environmental risks.

The increased percentage of metal removed from the organic fraction by EDDS followed the order of Cd > Cr > Ca > Pb > Zn > Cu > As > Al > Ni > Fe, however, Mn and Mg were decreased by 1% and 5% respectively. The two largest increases in terms of percentage induced by EDDS were Cd and Cr (76% and 41% respectively). The remaining metals ranged from 6% to 34% except Mn and Mg. The increased percentage of metal removal (data listed on the 5th column from the left in table 3-6) revealed that the heavy metals Cd, Cr, Pb, Zn, Cu, and As in organic fraction can be mobilized efficiently from the soil by adding EDDS into the mobilizing solution, whereas the amount (not percentage) of metals removed from the organic fraction (which is listed on the right-hand column of Table 3-6) suggested that Fe and Al were the two metals which were mainly responsible for releasing PAH compound (B[a]P) from the organic fraction. The sum of the quantity of Fe and Al accounted for 90% of total metals removed from the organic fraction. The relationship between PAH compound mobilization and Fe and Al will be discussed in detail in a subsequent section.

The heavy metals that remained with the soil particulates fraction after five successive soil washings by the two mobilizing solutions are presented in Table 3-7.

In the original soil, all heavy and trace metals were elevated above the federal norms. After soil washing in the presence of EDDS, the levels of Zn and Ni that remained with the soil conformed to maxima recommended by the Canadian Council of Ministers of the Environment (CCME) guidelines, and all other metals (Cd, Cr, and Pb) except As and Cu had been decreased to below or close to the limits for industrial or commercial use. By contrast, As and Cu remained well above the CCME guidelines.

Table 3-7. A comparison of trace metals left in soil residues with that of legislative norms.

Metal residues remaining with the soil particulates			CCME[a] Guidelines ($\mu g\ g^{-1}$)			
	Post SF washing	Post SE washing	Agr[b]	Residential / Parkland	Ind[c]	Comm[d]
As	290 ±32	244 ±22	12	12	12	12
Cd	38 ±3	18 ±2	1.4	10	22	22
Cr	132 ±11	90 ±8	64	64	87	87
Cu	516 ±38	401 ±26	63	63	91	91
Ni	45 ±3	40 ±4	50	50	50	50
Pb	475 ±46	274 ±22	70	140	600	260
Zn	231 ±24	173 ±16	200	200	360	360

[a] Canadian Council of Ministers of the Environment (CCME), 2007 [135]. Canadian soil quality guidelines for the protection of environmental and human health: Summary tables. Updated September, 2007. Canadian Council of Ministers of the Environment, Winnipeg. Available from http://www.ccme.ca/assets/pdf/rev_soil_summary_tbl_7.0_e.pdf ; [b] permissible residues in soil destined for agricultural use; [c] permissible residues in soil destined for industrial use; [d] permissible residues in soil destined for commercial use.

In summary, EDDS was effective at mobilizing both trace metals and PAH compounds. Cd was the most efficiently removed among the twelve metals studied, and Cr was the next. The high removal efficiencies of Cd and Cr by EDDS probably resulted from both their low contents in the soil and their relatively higher affinity for EDDS. In addition to Cd and Cr, Pb, Zn, and Cu were also removed efficiently by EDDS in comparison with the control surfactant solution. Ca was characterized by a higher removal percentage by EDDS than other cations due to 1) its much lower content (1330 μg g^{-1} soil) in the organic fraction in comparison with other cations Fe (115627 μg g^{-1} soil) and Al (6625 μg g^{-1} soil) in the organic fraction; 2) the inefficient extracting ability of control solution in organic fraction for Ca (15 μg g^{-1} soil of Ca was removed from organic fraction, which accounted for 1% of total). The combination of these two factors made the extraction of Ca in terms of percentage by EDDS look somewhat higher, but the quantity of Ca removed remained as lot smaller (472 μg g^{-1} soil) when compared with Fe (8025 μg g^{-1} soil) and Al (1520 μg g^{-1} soil) in organic fraction.

Although the percent removal of Fe and Al were not high (6% and 20% respectively), they represented the majority of EDDS complexes. Of the total metals removed from the organic fraction, 76% was Fe, and Al was accounted for a further 14%. The other metals collectively accounted for the remaining 10%. Clearly, within the organic fraction of the soil, Fe was the predominant metal that linked macromolecules of organic matter together and was responsible for maintaining this polymer in the solid phase. Aluminum also contributed to this behaviour.

3.2.2. EDDS *vs.* EDTA and pH effect on PAH mobilization

In a preliminary study, PAH mobilization efficiencies in the presence of EDDS or EDTA were compared. The results revealed that the EDDS-surfactant combination was somewhat more efficient (10%-15%) than the EDTA-surfactant combination at mobilizing PAH compounds. The studies were performed under the original EDDS/EDTA solution pH without adjustment. In order to gain some insights into the mechanism of EDDS enhancement on PAHs mobilization, two solution pHs were chosen: pH 6 and pH 9. The pH 6 value approximated the original pH value of 0.05 M EDTA - 3% (V/V) Brij98 solution, and the pH 9 value approximated the original pH of 0.05 M EDDS - 3% (V/V) Brij98 solution. In order to compare their efficiencies under the same pH condition, each of the solutions (0.05 M EDDS - 3% Brij98 and 0.05 M EDTA - 3% Brij98) was adjusted to one of the two pH values (pH 6 or pH 9). At the same time, a companion trial was performed in which various pHs (ranging from 5 to 9) of the 0.05 M EDDS-3% Brij98 solution were investigated to evaluate the influence of pH on EDDS performance. The results of EDDS *vs.* EDTA trials are summarized in Figures 3-3 and Figure 3-4.

The results indicated that 1) EDDS was more efficient than EDTA at mobilizing both chrysene and B[a]P; and 2) EDDS was more efficient at pH 9 than at pH 6. In contrast, EDTA did not display any appreciable difference with respect to pH. Relative to EDTA, EDDS removed 8% more B[a]P and 9% more chrysene from the soil with a single wash at pH 9. At pH 6, the extraction efficiencies for both B[a]P and chrysene with either EDTA or EDDS were not perceptibly different.

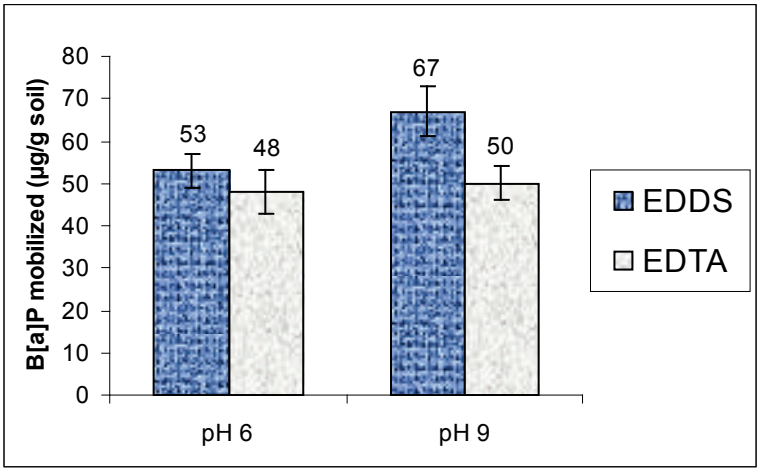


Figure 3-3. Comparison between EDDS and EDTA on B[a]P mobilization/removal.

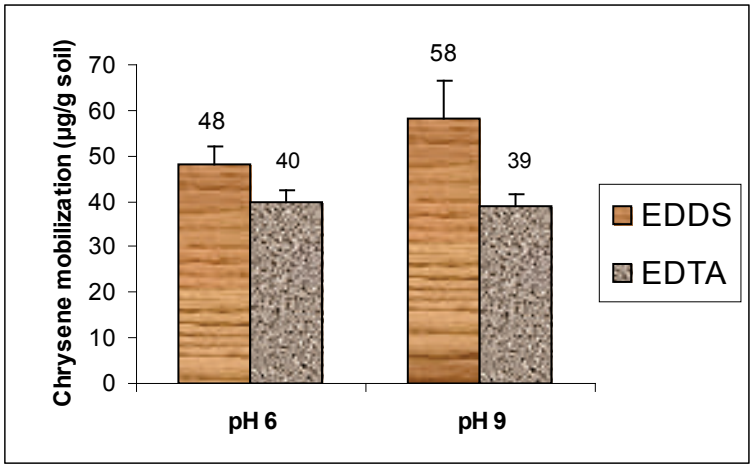


Figure 3-4. Comparison between EDDS *vs.* EDTA on chrysene mobilization.

These observations are similar to the previous studies on B[a]P and chrysene recoveries with these two chelating reagents [111], except that the difference of the recovery efficiencies for B[a]P between EDDS and EDTA was less pronounced. During the studies, the pH values of the soil slurries were measured just after adding the soils into each mobilizing solution. Figure 3-5 indicates the pH changes of the soil slurry from the original solution pH. The soil pH was 3.5. After adding the acidic soil, both EDDS soil slurries (original solution pH 6 and pH 9) did not change

appreciably (one from 6 to 5.99, and the other from 9 to 8.82); whereas the changes in pH of EDTA slurries decreased substantially. The soil slurries prepared from EDTA were decreased to 5.69 (initially at pH 9) and 5.26 (initially at pH 6). The pH variations between the two chelating reagents indicated that EDDS and EDTA had different buffering capacities. The difference in buffering capacity was observed repeatedly when attempting to adjust the pH of the mobilizing solutions generated with EDDS or EDTA. The same amount of acid or base (in drops) caused several units of pH change in EDTA solutions, but very small changes in EDDS solutions. The difference in buffering capacity between EDDS and EDTA might have resulted from differences in their stereo-chemical structures.

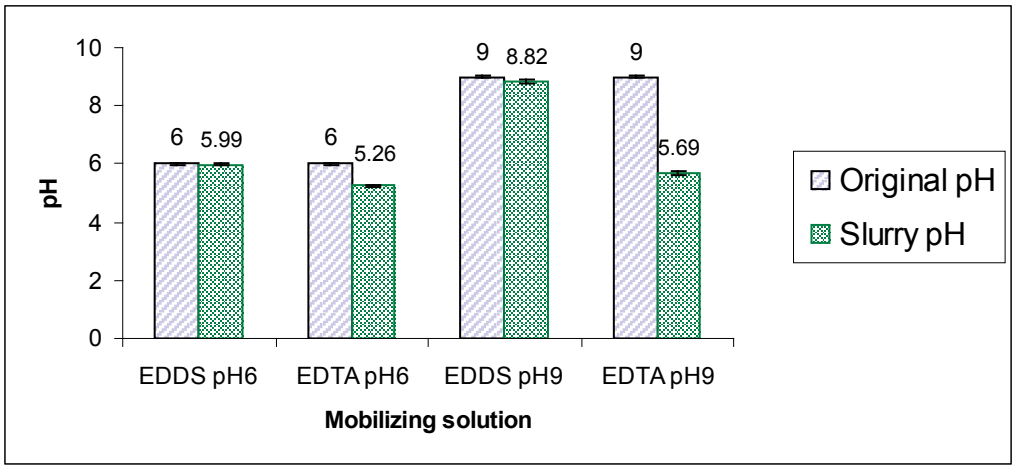


Figure 3-5. Differences in the pHs of the soil slurry (post equilibration) and the original mobilizing solution.

The initial form of EDDS was the trisodium salt (Na_3HEDDS), whereas the EDTA was the disodium salt (Na_2H_2EDTA). So the pH of EDDS initial solution (~pH 9) was different from that of EDTA (~pH 6), which was in agreement or similar with the values reported in literatures (Table 3-8) [136, 137]. Although both compounds have four carboxylate groups per molecule, and the stability constant values between

EDDS and EDTA are similar (with higher values of EDDS when in the forms of $H_2L^{2-} \rightarrow H_4L$), the carboxylate groups may exert different influences on the free H^+ addition in solution when they are in metal-complex form due to their different three-dimensional arrangement in space. When complexing metal ions, the four carboxylate groups of EDDS tend to bend closer to each other and stay almost on the same plane or on one side of the molecule, and leave the protons of the molecule on the other side (Figure 3-6, C).

Table 3-8. The stepwise stability constants of EDTA and [*S,S*]-EDDS.

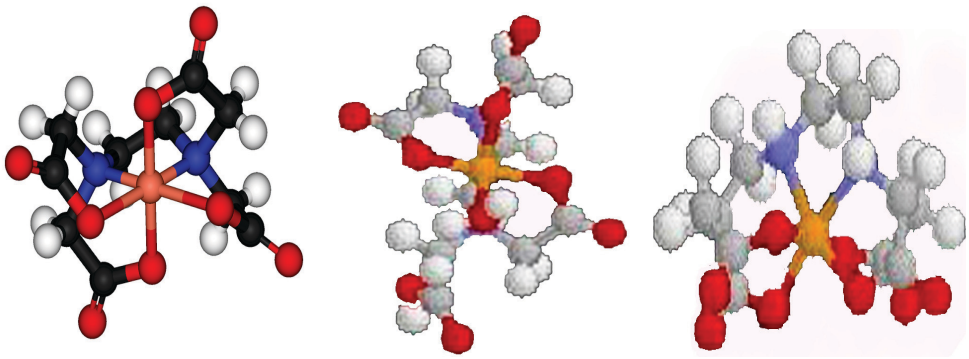
Reaction	Log *K* EDTA[a]	Log (K +3σ) [*S,S*]-EDDS[a]	EDDS[b]	EDTA[b]
$L^{4-} + H^+ \rightarrow HL^{3-}$	9.5-10.4	10.1 ±0.1	9.8	10.4
$HL^{3-} + H^+ \rightarrow H_2L^{2-}$	6.13	6.91 ±0.02	6.8	6.4
$H_2L^{2-} + H^+ \rightarrow H_3L^-$	2.69	3.84 ±0.02	3.9	3.0
$H_3L^- + H^+ \rightarrow H_4L$	2.00	3.05 ±0.02	2.4	2.1
$H_4L + H^+ \rightarrow H_5L^+$	1.5	1.4 ±0.2		
$H_5L^+ + H^+ \rightarrow H_6L^{2+}$	0.0	2.1±0.2		

[a] [136] M. Orama, H. Hyvonen, H. Saarinen, and R. Aksela, Complexation of [*S,S*] and mixed stereoisomers of *N, N*' ethylenediaminedisuccinic acid (EDDS) with Fe, Cu, Zn, and Mn ions in aqueous solution, J. Chem. Soc., Dalton Trans., 2002, 4644-4649.

[b] [137] P. C. Vandevivere, H. Saveyn, W. Verstraete, T. C. J. Feijtel, and D. R. Schowanek, Biodegradation of metal-[*S,S*]-EDDS complexes, Environ. Sci. Technol., 35, 2001, 1765-1770.

In all the three figures (Figure 3-6 A, B, and C), white spheres represent protons, red spheres designate oxygen atoms, and darker grey (or black), blue, and orange spheres represent carbon, nitrogen, and Cu or Fe atoms respectively. When free protons (H^+) in solution approach oxygen on the carboxylate groups, there might be little (or at least less) repulsion force coming from the protons on the EDDS molecule. In other words, there is a stronger negative field around the four oxygen

atoms of the carboxylate groups of EDDS, which not only attracted free protons more strongly and holds them in place, but can also attract more protons around them by electrostatic attraction. In the case of EDTA, the four carboxylate groups are oriented in all directions and are surrounded by the protons of the molecule (Figure 3-6, A and B).



A. $[EDTA\text{-}Cu]^{2-}$ complex B. $[EDTA\text{-}water\text{-}Fe]^{-}$ complex C. $[EDDS\text{-}Fe]^{-}$ complex

Figure 3-6. The stereo-arrangement of EDDS and EDTA complexes [138].

The protons around oxygen atoms may repel the free protons from the solution. Or put another way**,** the protons near the oxygen atoms cancel out some of the negative field strength and weaken the attractive force of oxygen for free protons. As a result, 1) the protons linked to the oxygen atoms on EDTA were not as stable as the ones on EDDS and may be easily freed into the solution; 2) the number of protons around oxygen atoms on EDTA may also be less then that on EDDS. This might explain, in part, the differences in buffering capacity between EDTA and EDDS.

Please note that the responses in Figure 3-3 (B[a]P extracted), Figure 3-4 (chrysene extracted) and Figure 3-5 (pH changes in soil slurry) were matched well. If these three sets of data are plotted on the same graph, Figure 3-7 results. The unit of B[a]P and chrysene on the graph was expressed as $\mu g\ 0.1 g^{-1}$ soil which was adjusted

to match the plotting scale of pH values in the soil slurry. The congruency of the three lines in Figure 3-7 suggests that variations in mobilization efficiency mirror the changes in pH. The soil slurry pH was well matched with the amount of PAH recovered from the soil. Clearly, the pH of the extraction played a key role in mobilizing PAH compounds during soil washing. An increased pH resulted in higher PAH recovery, and lower pH decreased the PAH recovery.

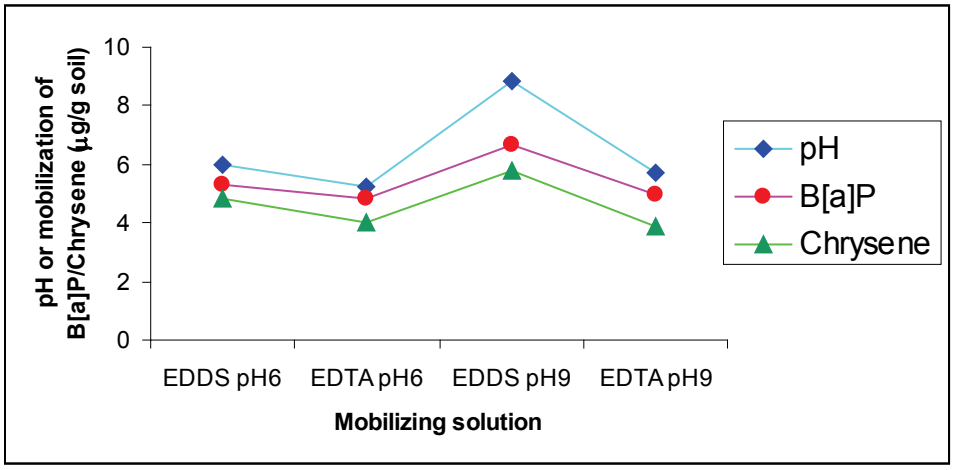


Figure 3-7. The similarity between pH change in soil slurry and PAH recovery.

The results of pH trials further corroborated the findings regarding the relationship between pH and PAH remediation efficiency. Figure 3-8 suggested that B[a]P mobilization by 0.05 M EDDS-3% (V/V) Brij98 mobilizing solution was a function of pH. For the range of pH between 5 and 9, the recovery of B[a]P increased steadily from pH 5 to 8. At pH 9, the amount of B[a]P was decreased slightly (but not significantly). Chrysene extraction by various pH solutions displayed a similar trend with a slight variation, *i.e.* the highest amount extracted at pH 7, and afterwards the recovery amount decreased slightly with the increasing of pH (Figure 3-9).

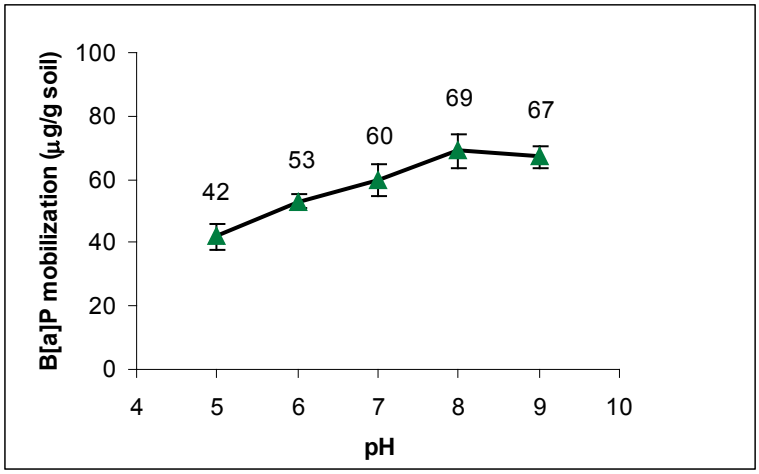


Figure 3-8. pH effects on B[a]P mobilization by EDDS.

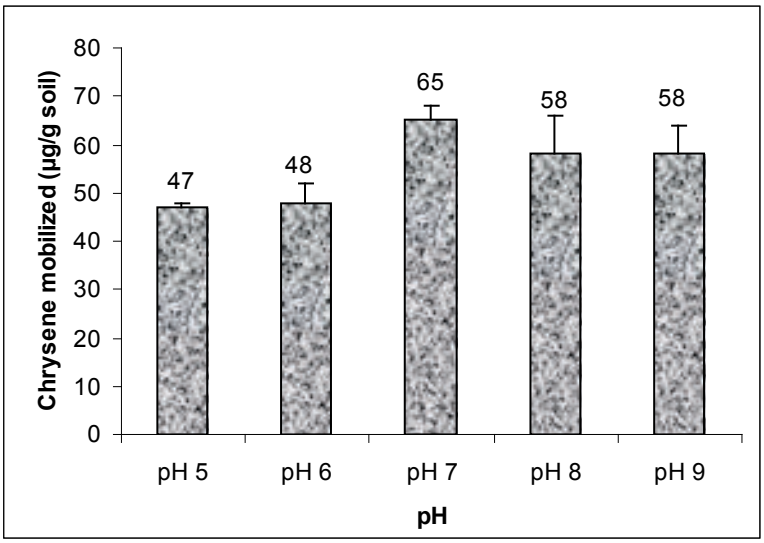


Figure 3-9. pH effect on chrysene remobilization.

In general, pH did play an appreciable role in PAH mobilization. Higher pH resulted in higher extraction efficiency. At pH 8, 29% of B[a]P was removed from the soil with a single soil equilibration; whereas at pH 5, the removal rate was decreased to 18%. Chrysene was mobilized more readily at alkaline pH than within the acidic range. However, the optimal pH for chrysene proved to be at neutral pH.

Figure 3-10 displays the colour differences between various pH extracts of 0.05 M EDDS-3% (V/V) Brij98 solution, which resulted from overnight reaction in the absence of shaking or sonication. The solution pHs from left to right were 5, 6, 7, 8, or 9. The colour gradient suggested that dissolved organic matter increased with the increasing of solution pH. The solution of pH 9 resulted in the darkest color and the solution of pH 5 provided the lightest one.

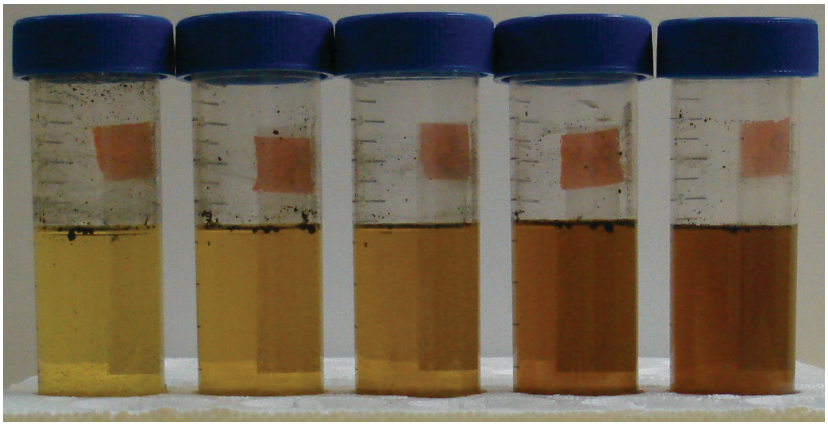


Figure 3-10. The colour difference among EDDS extracts with various pH values.

At the beginning of the pH trials, seven metals (Fe, Al, Ca, Pb, Cu, As, and Zn) that collectively comprised 98% of total metals extracted from the organic fraction in the previous study were analyzed. The results were not surprising. Most of the metals (except Cu and Ca) were characterized by higher recovery rates at lower pH values than that at higher pHs reflecting the general trend of greater solubility in more acidic media. The data are presented in Table 3-9. To understand the phenomenon, sequential extractions were performed subsequent to fractionation of the metals into three components: exchangeable, reducible, and oxidizible. The results demonstrated that the increased quantities of metals by acidic mobilizing solutions mainly came from the reducible fraction of the soil, and to a lesser extend from the

exchangeable fraction (data not show). For the organic fraction, all of the metal recoveries increased with the increasing solution pH (Table 3-10).

Table 3-9. Total metal (μg g^{-1} soil) extracted from the soil with 3 % (V/V) Brij98 in 0.05 M [*S,S*]-EDDS at various pHs.

pH	Fe	Al	As	Ca	Cu	Pb	Zn
5	11177 ±342	1303 ±45	39 ±3	1566 ±32	83 ±2	81 ±3	148 ±7
6	1036 ±6	1255 ±26	34 ±1	1557 ±45	84 ±2	84 ±2	145 ±3
7	8003 ±544	1128 ±53	23 ±2	1780 ±14	87 ±1	80 ±1	137 ±2
8	6793 ±275	1133 ±30	17 ±3	1791 ±13	87 ±2	84 ±3	141 ±2
9	6435 ±122	1112 ±9	22 ±3	1768 ±9	89 ±1	80 ±1	134 ±3

Table 3-10. Metals (μg g^{-1} soil) extracted from organic fraction with 0.05 M [*S,S*]-EDDS in 3 % (V/V) Brij98 solution at various pHs.

pH	Fe	Al	Cu	As	Ca	Zn	Pb
5	1731 ±165	350 ±22	35 ± 1	6 ± 1	154 ±11	21 ±2	33 ±3
6	2177 ±211	445 ±32	46 ± 2	9 ± 1	155 ±12	26 ±3	42 ±2
7	2372 ±200	500 ±53	53 ± 1	11 ± 1	174 ±14	29 ±1	47 ±2
8	2745 ±221	549 ±34	58 ± 2	14 ± 1	196 ±13	32 ±2	55 ±3
9	2800 ±209	566 ±50	60 ± 2	16 ± 1	194 ±9	33 ±2	61 ±2

3.2.3. Proposed mechanisms

By linking all the data from this series of trials, a mechanism is now proposed to account for the [*S,S*]-EDDS enhancement of B[a]P removal in surfactant- based aqueous washing solution. EDDS, as a chelating reagent, has been recognized to have equal or higher efficiencies for removing metal ions from soils. The ability of

EDDS to appreciably increase B[a]P recovery in these studies could not have been accomplished through a direct contact/reaction with B[a]P, for it has not been recognized as a surface active agent and has little detergency to increase the partitioning process of B[a]P from soil particulate surfaces into the mobilizing solution. One way for EDDS to influence B[a]P dissolution is indirectly through increased metal extractability. The mechanism of EDDS enhancement on B[a]P removal in surfactant- based aqueous washing solution is postulated to be as follows.

First, the higher buffering capacity of EDDS that resulted, in part, from the three-dimensional arrangement of the four carboxylate groups was the key factor which affected the behaviours of three types of materials in washing solution — EDDS itself, soil organic matter, and surfactant. When the initial solution pHs were all ~9, only EDDS maintained the solution pHs high in the alkaline range (pH 8-9) during soil equilibrations, whereas surfactant and EDTA pHs decreased either to below 4 or to below 6 (Table 3-4 and Figure 3-5). The increased solution pH of EDDS had three perceptible effects on the soil washing process. Firstly, 1) the quantity of Fe and Al extracted from the soil organic fraction by EDDS increased considerably with the increasing solution pH (Table 3-5 and Table 3-6); the similar observations were also found by other researchers [23, 25-27, 37]. Secondly, the enhanced removal of Fe and Al from their bridging positions between macromolecules within the organic fraction by EDDS caused the collapse of the rigid frame of the organic network. This collapse was more extensive in the case of EDDS than for either surfactant or EDTA, which resulted in more organic matter dissolution into the washing solution. The phenomenon of higher pH resulted in more organic matter dissolution has also

been observed in the current studies (Figure 3-1, Figure 3-2, and Figure 3-7) as well as by numerous other researchers [25-28, 31, 37]. The enhanced process of organic matter dissolution was accompanied by an increased B[a]P release from the soil organic fraction for several reasons. Firstly, B[a]P molecules that were attached to the DOM fraction were released into solution as a result of DOM solubilisation; secondly, DOM functioned as a surfactant in solution [123-126, 129] which enhanced B[a]P partitioning process once the blockages of Fe and Al had been removed. Once removed, pathways for B[a]P mass transfer into solution [24] became operative; furthermore, DOM in solution also served as chelating reagents [38, 39, 45, 46] which, in tern, increased the extractability of Fe and Al; moreover, at higher pH, the adsorption of surfactant decreased [122], which added more micellar capacity into the washing solution and enhanced the mass transfer process of B[a]P from the soil particulate phase into the aqueous phase. All of the positive influences described above caused by increased buffering capacity of EDDS led ultimately to a gain in B[a]P removal when compared to either EDTA or surfactant.

3.3. The determination of operating variables

The operating variables included pH (which, for convenience, was discussed in the previous section), the duration of the ultrasonication, concentrations of EDDS and surfactant (Brij98), metal removal from the recovery solutions, and solution to soil ratio.

3.3.1. Duration of ultrasonication

Figure 3-11 presents the influence of the ultrasonication time on B[a]P recovery in 0.1 M EDDS- Brij98 (6%, V/V) solution. The application of high intensity energy in the form of ultrasonic waves was aimed at disrupting aggregates within the soil as well as the relatively weak interaction forces between contaminants and the soil particle surfaces so to achieve an enhanced contact between the mobilizing solution and the contaminants. Figure 3-11 suggested that the mobilization of B[a]P was a

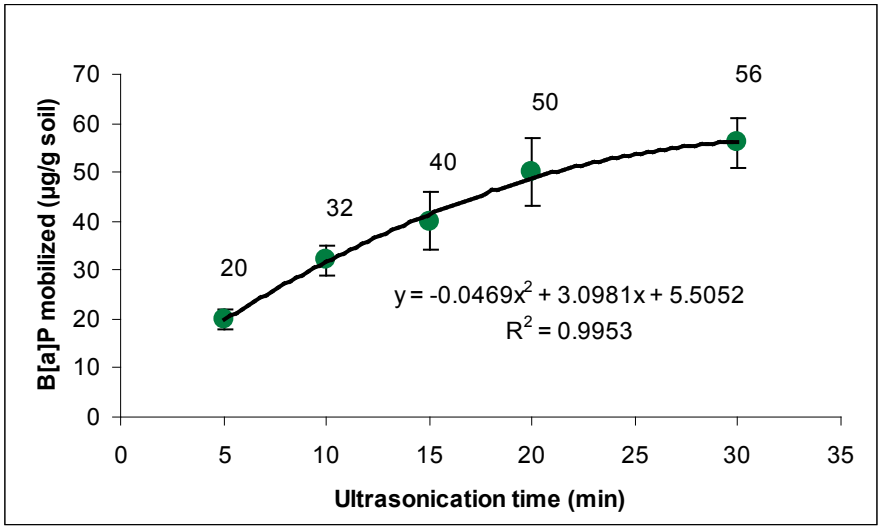


Figure 3-11. Duration of ultrasonication effect on B[a]P recovery.

quadratic function of the ultrasonication time. A longer time of ultrasonication resulted in an increased recovery of B[a]P. The quantity of B[a]P mobilized after 30 min of agitation reached the plateau within the curve. B[a]P recovery after 30 min of sonication was 1.8-fold higher than after 5 min, 75% higher than after 10 min, 40% higher than after 15 min, and 12% higher than after 20 min. By analyzing the two major metals Fe and Al, which comprised 90% of total metals extracted from the soil organic fraction and served as linkages between the macromolecules of organic matter, insights can be gained for the relationship between ultrasonication

time and B[a]P mobilization. Figure 3-12 and Figure 3-13 demonstrate that the quantities of Fe and Al extracted from the soil were quadratic functions of the ultrasonic time. Both Fe and Al extraction efficiencies had reached maxima by 30 min. It should be pointed out that the quantities of Fe and Al in Figure 3-12 and Figure 3-13 represent the total quantities of Fe and Al extracted from the whole soil profile, and not only the organic fraction. However, because of the extraction solutions were all the same, we can presume that the proportions mobilized by

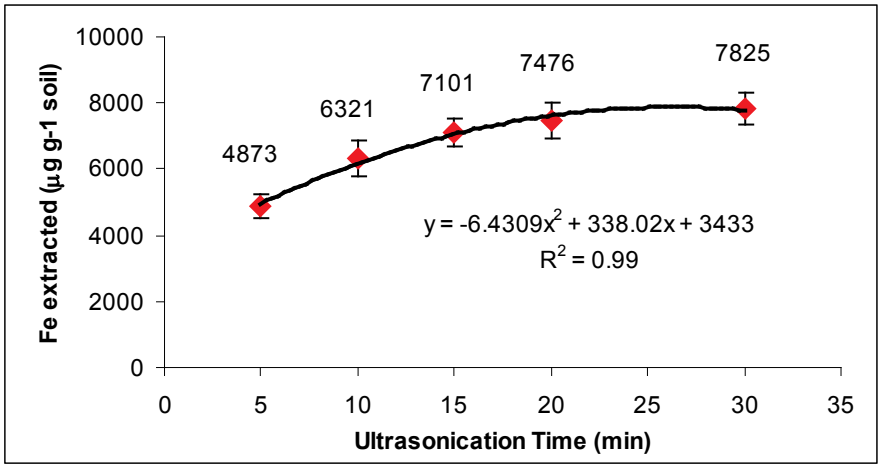


Figure 3-12. Fe extraction as a quadratic function of ultrasonic time.

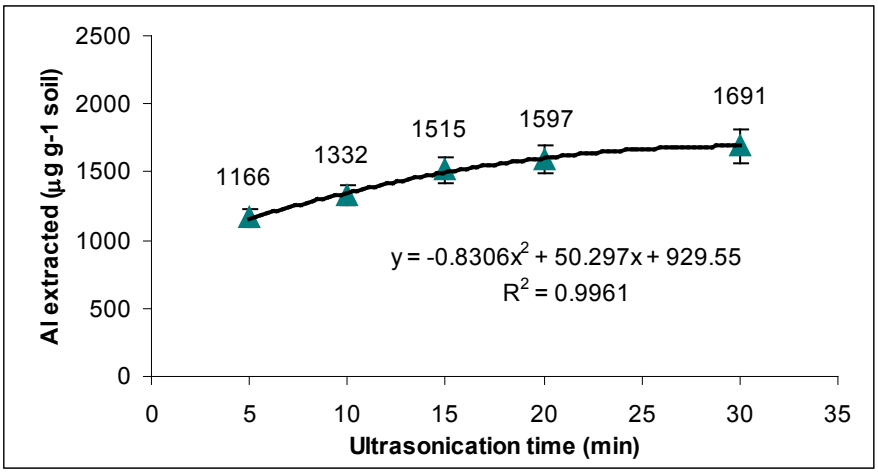


Figure 3-13. Al extraction as a quadratic function of ultrasonic time.

various ultrasonication times from the organic fraction would be similar for Fe or Al. The Fe and Al extracted from the soil organic fraction is anticipated to increase in proportion to the increasing ultrasonication time. If Figure 3-11 Figure 3-12 and Figure 3-13 are compared, the trends for all graphs are similar — the recoveries of the three analytes are all quadratic functions that increase with increasing ultrasonication time and suggests that B[a]P mobilization from the soil is closely associated with the extraction of Fe and Al.

In addition to Fe and Al, the extractions of the other analyte metals all increased with the increased ultrasonication time (data not show). The increased percentage of analyte metals between 5 min and 30 min ranged from 0.4% to 61% and followed the order of Fe (61%) > Cr (60%) > Al (45) > Cd (43%) > As (38%) > Cu (17%) > Zn (15%) > Pb (14%) > Mn (5%) > Mg (4%) > Ca (0.4%). Ultrasonication time had an appreciable influence on Fe, Cr, Al, Cd, and As extraction, but had almost no perceptible effect on Ca.

3.3.2. Critical Micelle Concentration (CMC) determination

The CMC of the surfactant (Brij98) has been reported to be at 3% [19, 111]. By adding 0.05 M EDDS, the CMC of the surfactant solution was decreased considerably (Figure 3-14). From the shape of the curve in Figure 3-14, it can be observed that 3% was no longer the CMC point of Brij98, and the new CMC of the surfactant with EDDS presence was decreased to somewhere between 1.5 and 3%. The decreased CMC of the surfactant solution might have resulted mainly from the relatively high pH during equilibrations with soil because of the presence of EDDS. As discussed

previously, solutions in the presence of EDDS were characterized by a higher resistance to pH changes than in the presence of surfactant alone. The presence of EDDS maintained the mobilizing solution pH between 8 and 9 throughout the equilibration. Studies have suggested that the adsorption of surfactant decreased with increasing solution pH [122]. In addition to the CMC value, Figure 3-14 also revealed that the increases B[a]P mobilization continued when the Brij98 concentration exceeded 3%. Although the slope above 3% became less steep, the 6% Brij98 solution showed a considerably higher B[a]P mobilization capacity than the 3% solution (22% higher) and the 4.5% solution also increased the B[a]P mobilization (8% higher, data not shown).

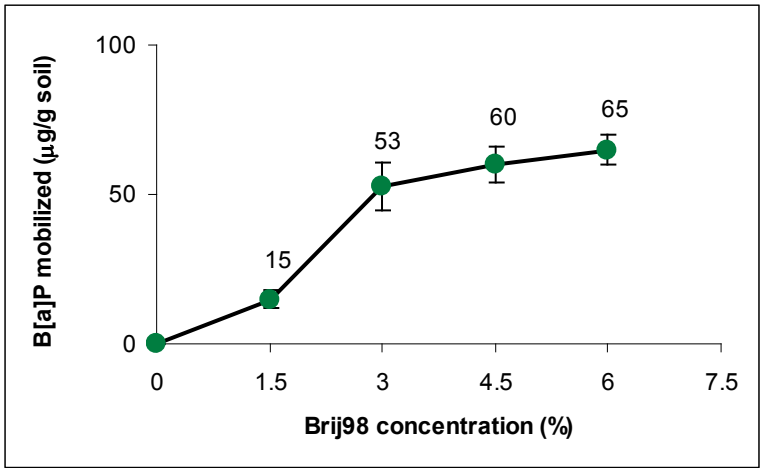


Figure 3-14. Surfactant concentration effect on B[a]P mobilization.

The results of EDDS concentration study are presented in Figure 3-15. The 0.10 M EDDS solution provided the greatest quantity of B[a]P mobilization. The EDDS concentration above 0.10 M did not provide further increases in B[a]P removal with further increased concentration. In fact, 0.15 M was observed to be the highest

EDDS concentration to result in a clear solution in 3% Brij98 solution. As the concentration of EDDS (in 3% (V/V) Brij98 solution) approached 0.20 M, turbidity within the solution became apparent. It seemed that EDDS, at higher concentration, caused the precipitation of one or more of the components. Although the mechanism remains unclear, the phenomenon may help to explain the slight decrease of B[a]P mobilization by 0.15 M EDDS-3% (V/V) Brij98 solution, *i.e.* small colloidal aggregates of the surfactant might have started to form in 0.15 M EDDS-3% (V/V) Brij98 solution.

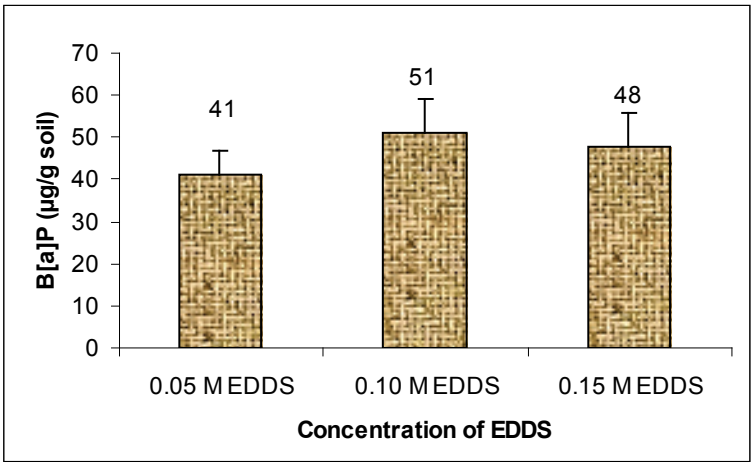


Figure 3-15. The effect of EDDS dosage on B[a]P removal.

3.3.3. Metal ion clean-up

The purpose of removing heavy and trace metal ions from the recovery solution was to free up EDDS molecules from their metal-EDDS complexes, so that more contaminating metal ions could be removed from the soil during subsequent equilibrations with recycled washing solution. An increased number of washing cycles were anticipated to increase the net mobilization of B[a]P and chrysene. The results were not surprising. B[a]P mobilized by the recovered solutions (with metal

removal) did not provide any increase in comparison with the control solution (absence of metal clean-up). Figure 3-16 and Figure 3-17 present the effects of metal clean-up on B[a]P and chrysene mobilization. Within experimental error, the recoveries of PAH compounds after the initial equilibration and after each recycle were the same.

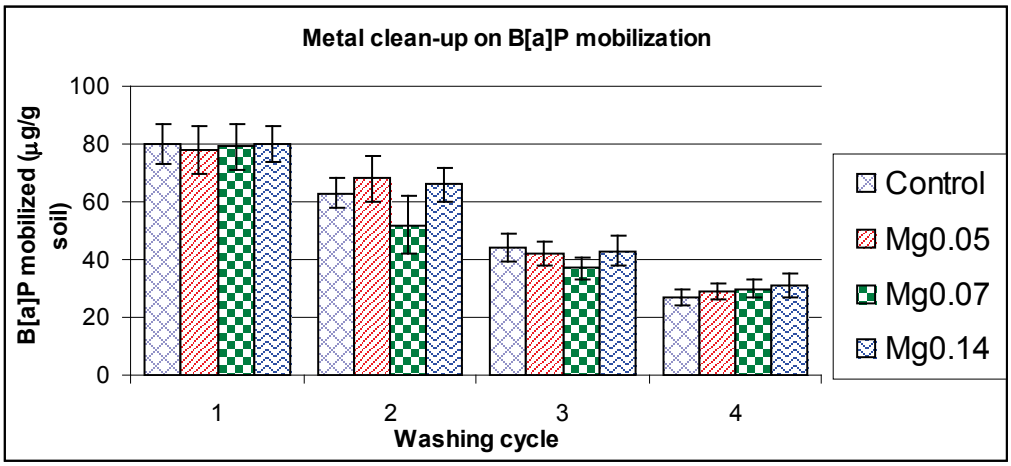


Figure 3-16. Effect of metal clean-up on B[a]P mobilization.

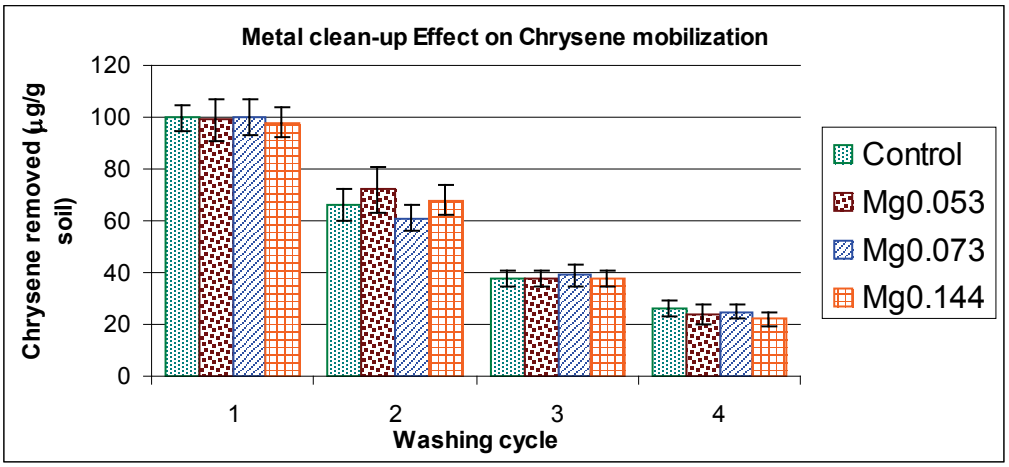


Figure 3-17. Effect of metal clean-up on chrysene remobilization.

The Mg^0 flakes (0.053 g, 0.073 g, or 0.144 g) were hydrolyzed spontaneously in the aqueous medium and liberated hydroxide ion that combined with metal ions to form insoluble oxide/hydroxide precipitates. The results did not detect any appreciable differences in PAH content between the control solution (the solution recovered without zero-valent magnesium (Mg^0) treatment) and the treated cleaned solution (after the heavy and trace metal ions had been replaced by magnesium ion), suggesting that the two solutions contained equal quantities of PAH compounds. It was concluded that the treatment with Mg^0 flakes did not affect the mobilization/recovery of PAH compounds adversely.

The percentages of metals that remained with the soil particulate fraction after four sequential extractions are summarized in Table 3-11. The trace and heavy metals that remained with the particulates following treatment with zero-valent magnesium (Mg^0) were considerably decreased relative to control extractions for some elements. Treatment with Mg^0 acted as a source for the controlled release of hydroxide ion to precipitate the target metals as insoluble oxides / hydroxides.

Table 3-11. Metals (%) that remained with the particulate fraction post four sequential washings with recycled EDDS-Brij98 solution.

Treatment	Al	As	Ca	Cd	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Zn
Control	83	70	45	46	67	73	89	78	94	73	44	45
0.053g Mg^0	83	34	45	23	48	26	86	196	90	69	87	36
0.073g Mg^0	85	22	47	43	52	30	90	243	99	103	100	45
0.144g Mg^0	84	17	46	-5	43	27	88	276	92	65	97	46

The controlled release of hydroxide was considered to benefit the removal process because the particles of solid product were coarser and more readily filtered. Frequently, metal precipitations with hydroxide solutions result in sols / gels that are very difficult to filter. The subsequent removal of the solids from the extract was readily accomplished by filtration. The complexing reagent, present as EDDS-Mg complex and the Brij98 surfactant remained with the liquid supernatant phase.

The removal efficiencies (expressed relative to the original soil concentration) for the control wash and for treatment with three quantities of Mg^0 are summarized in Table 3-12. Although the removal efficiencies for most trace metals were increased (As, Cd, Cr, and Cu), cation ions (Al, Ca, Fe, Mn) and two trace metals (Ni and Zn) were relatively unaffected and one (Pb) was decreased appreciably.

Table 3-12. Metal extraction efficiencies (expressed as % removed from the soil).

	Al	As	Ca	Cd	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Zn
Control	17	30	55	54	32	27	11	22	6	27	56	55
0.053gMg^0	17	66	55	77	52	74	14	-96	10	30	13	64
0.073gMg^0	15	78	53	56	48	70	10	-143	1	-4	-0.5	55
0.144gMg^0	16	83	54	105	57	73	12	-176	8	34	3	54

The fact that the percent removal of cation ions were unaffected by Mg^0 treatment might have resulted from their high content in the soil (*e.g.* Al, Fe, and Mn) or increased solubility of the hydroxide (*e.g.* $Ca(OH)_2$). As to trace metals, Cu has been recognized by numerous studies to have the highest affinity for EDDS among divalent metal ions. Under EDDS deficiency, Cu out-competed Zn, Pb and Ni for

EDDS resulting in increased Cu removal at the expense of other ions (Zn and Ni) or decreased (Pb). The decreased Pb recovery might also have resulted from the formation of anionic hydroxide complex ($Pb(OH)_3^-$. As a result, Pb remained in the washing solution as soluble anions and recombined with the EDDS when re-acidified.

3.3.4. Solution to soil ratio effect

Two solution/soil ratios were studied: 6.6 and 3.3. The 6.6 ratio represented a convenient ratio that has been employed for several years for studies performed with 1-3 g samples of soil. The 3.3 ratio was chosen based on the findings of Yin *et al.* [43]. According to Yin., with increasing pH and decreasing solution volume, the surfaces of soil particles became increasingly deprotonated and the repulsions between the negatively charged particles (SOM) increased dramatically. The decreased space between the soil particles resulted in an increased colloid formation. The colloid was demonstrated to be DOM-carrying metal ions. Correlation analysis indicated that the appreciable increase in Cu mobilization with decreasing solution volume at high pH was strongly associated with the increased colloid formation of soil organic matter (SOM, *i.e.* desorption of SOM). Yin *et al.* also pointed out that the dispersion of particles (colloid formation) was very limited at lower pH values [43].

The results of solution/soil ratio study are illustrated on Figure 3-18. The columns on the left represent chrysene mobilization in terms of quantity (μg g^{-1} soil) and the columns on the right indicate the percent mobilization relative to the total burden in

the soil. The results suggested that the solution/soil ratio 6.6 mobilized more chrysene (5% higher) from per gram of soil compared with the liquid to solid ratio of 3.3.

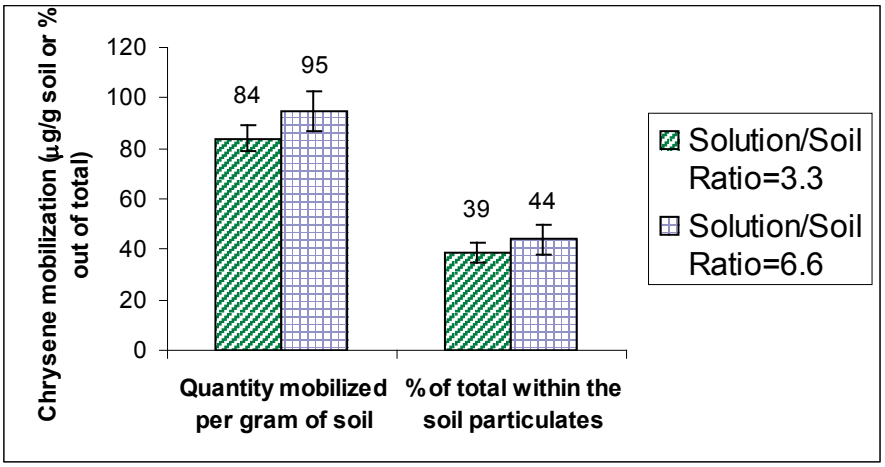


Figure 3-18. Solution/soil ratio effect on chrysene mobilization.

However, if the data are calculated based on the total amount of chrysene mobilized by the same amount of mobilizing solution or chrysene extracted by per mmol EDDS, the recovery efficiencies are reversed (Figure 3-19). In terms of total chrysene mobilized, the same volume of solution (20 ml of 0.1 M EDDS-6% Brij98) in ratio 3.3 mobilized 504 µg from 6 g soil; whereas only 285 µg chrysene was

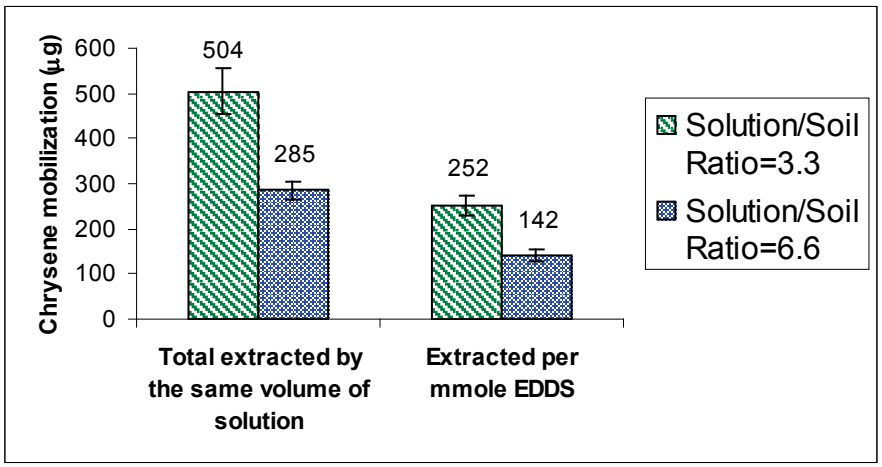


Figure 3-19. The effect of solution/soil ratio on chrysene mobilization.

mobilized by ratio 6.6 from 3 g soil. The ratio 3.3 mobilized more chrysene (77% higher), because the soil mass in ratio 3.3 was doubled in comparison with ratio 6.6. If chrysene mobilization was calculated based on per mmol EDDS, ratio 3.3 showed a higher recovery rate (252 μg/mmol EDDS) than ratio 6.6 (142 μg/mmol EDDS). Which solution/soil ratio was more effective depended on one's point of view: per gram soil, per mmol EDDS, or the volume of mobilizing solution. The solution/soil ratio 3.3 seemed more economic, because the same volume of solution removed 77% more chrysene in total. However, there were a number of operational problems or difficulties associated with the lower solution/soil ratio. The soil suspension was observed to foam readily during ultrasonication due to the higher proportion of soil. Because the soil mass was doubled and chrysene mobilization from per gram of soil was decreased slightly (5% less), the total chrysene that remained with the soil particulates after washing was greater (786 μg chrysene remained with the soil particulates after washing with the 3.3 ratio *vs.* 360 μg remained after washing with the 6.6 ratio). More washing cycles would be needed. The added expenses of increased energy, labour and more water, made washing with the 3.3 ratio less attractive.

3.4. Procedure evaluation

Based on studies of the operating variables of the soil washing system and procedure, the following parameters were adopted:

Soil washing system:

Aqueous washing solution contained 0.1 M EDDS in 6% (V/V) Brij98 at pH 9.

Mobilization procedure:

Soil, 3 g, was equilibrated with 20 ml of mobilizing solution (solution/soil ratio 6.6) in a 50 ml plastic centrifuge tube during 30 min in the presence of ultrasonic energy provided by the ultrasonic homogenizer. The detailed description regarding the ultrasonication procedure can be found in Section **2,2.3. Soil washing**. Post ultrasonication, the resulting suspension was centrifuged at 5000 rpm for 1 h. The soil supernatant fraction was back-extracted with hexane-MIBK mixture (9:1) to partition PAH compounds from the soil washes into the organic phase. The organic fraction (hexane-MIBK) containing PAH compounds was concentrated to 1 ml and stored in a refrigerator to await GC-MS analysis. The recovered aqueous solution that resulted from the back-extraction was used for the subsequent equilibration with the soil particulates phase, and the procedure (including equilibration, centrifugation, and back-extraction) repeated eight more times.

Post nine successive equilibrations, the solid soil phase was block-digested followed the procedure described in **Materials and Methods,** section 2.6. and 2.8., for block-digestion and metal analysis.

During the procedure evaluation studies, the optimized solution (0.1 M EDDS-6% Brij98, pH 9) was compared with two other mobilizing solutions (0.1 M EDTA-6% Brij98, pH 9 and 6% Brij98 alone, pH 9) for PAH compound mobilization as well as for heavy metal remediation. The soil washing procedure was performed with the

optimized conditions and repeated nine times. The results of B[a]P mobilization with the various mobilizing solutions are illustrated in Figure 3-20. The optimized washing solution is designated as **EDDS**, and the other two washing solutions are symbolized as **EDTA** and **Brij98** (or **control**).

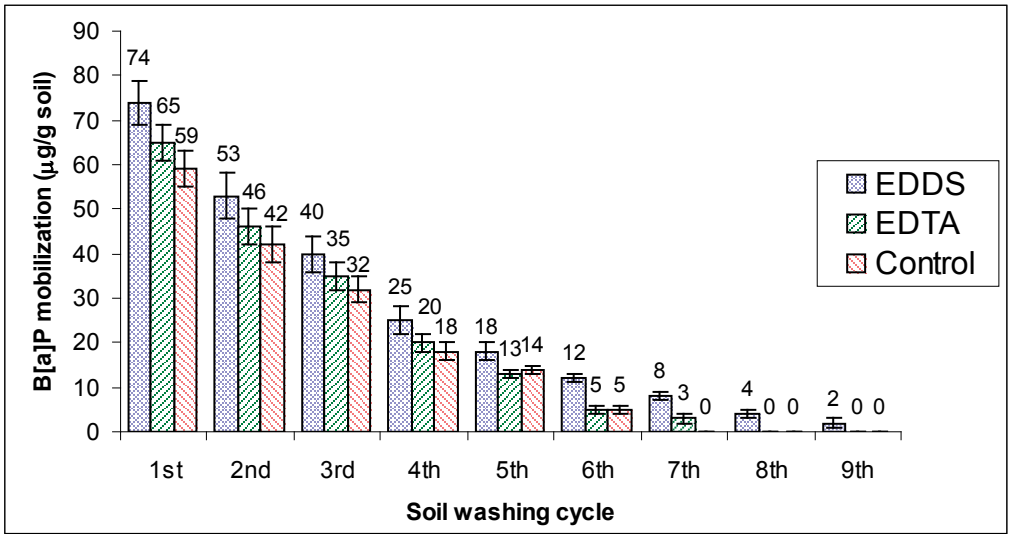


Figure 3-20. B[a]P mobilization by optimized procedure (EDDS) in comparison with that by EDTA and by control Brij98.

The mobilization efficiency of the EDDS washing solution was compared with efficiencies in the presence of an equivalent quantity of EDTA or in the absence of complexing reagent (surfactant Brij98 alone). The cumulative mobilization after nine washes in the presence of EDDS were more efficient at mobilizing B[a]P in comparison with EDTA or with surfactant alone. The EDDS treatment had extracted 101% of total B[a]P within the soil particulates after nine soil washing cycles, whereas EDTA and surfactant removed 80% and 73% respectively. The net increase of EDDS on B[a]P mobilization was 21% more than EDTA and 28% more than surfactant alone after nine sequential equilibrations. The EDTA treatment demonstrated some enhancement (7% higher) of B[a]P mobilization compared with the surfactant alone, although the extend of increase was not as great as for the

EDDS treatment. Not surprisingly, the B[a]P extracted from all three solutions decreased continuously during successive equilibrations. The control solution (surfactant alone) ceased to mobilize analyte after seven cycles, the EDTA-amended surfactant ceased after eight cycles and EDDS lasted for cycle nine. However, the variations of the measurements after nine equilibrations with EDDS were considerable, and the magnitude of the measurements was quite small. Perhaps, it was just a contamination from the previous run.

In contrast to B[a]P mobilization, chrysene recovery (Figure 3-21) by all three solutions were similar. No significant differences were found between EDDS, EDTA, and control solution with respect to chrysene recovery. Similar to B[a]P mobilization, the quantity of chrysene mobilized from all three solutions decreased continuously. However, the cumulative quantity of chrysene recovered in all three solutions was virtually quantitative: 100% with EDDS, 102% with EDTA, and 99%

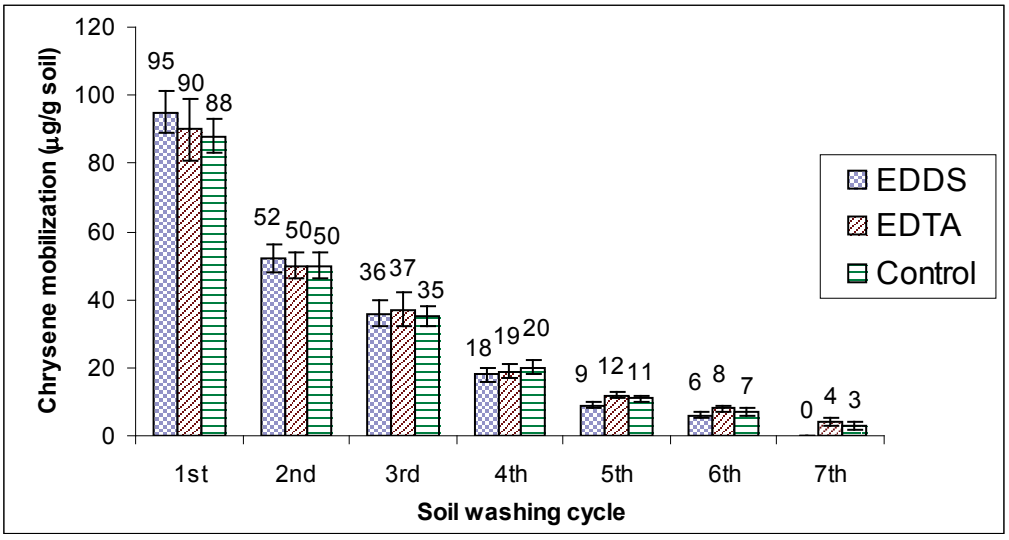


Figure 3-21. Chrysene mobilization by optimized procedure (EDDS) in comparison with that by EDTA and by control Brij98.

with surfactant. The similar and high mobilization efficiencies among the three washing solutions suggested that metal extraction in the presence of chelating reagent did not influence chrysene mobilization.

Determinations of PAH compounds that remained in the soil residuals after nine successive equilibrations were performed. The degrees of cleanness of the soil, in terms of PAH compound contamination, following the three treatments are presented in Table 3-13.

Table 3-13. PAH compounds remaining within the soil residuals post nine washes in comparison with CCME guidelines.

Compound	Treatment	Remaining in soil residuals ($\mu g\ g^{-1}$ soil)	LOQ* ($\mu g\ g^{-1}$ soil)	CCME[a] Guideline ($\mu g\ g^{-1}$ soil)			
				Agr[b]	Resi /Park[c]	Ind[d]	Comm[e]
Chrysene	Control	None detected	0.3	2.1	2.1	2.1	2.1
	EDTA	None detected					
	EDDS	None detected					
B[a]P	Control	60±4.8	0.2	0.6	0.6	0.6	0.6
	EDTA	46±3.2					
	EDDS	None detected					

[a] Canadian Council of Ministers of the Environment (CCME), 2008 [128]; [b] permissible residues in soil destined for agricultural use; [c] permissible residues in soil destined for residential/parkland use; [d] permissible residues in soil destined for industrial use; [e] permissible residues in soil destined for commercial use.

* Limit of Quantitation (LOQ) equals 10 times the standard deviation of the baseline noise divided by the slope of the calibration curve (it equals 3 times the estimated limit of detection).

Residues of both B[a]P and chrysene were not detected in the soil treated with EDDS. Considering the estimated Limit of Quantitation (LOQ), the results

suggested that EDDS treated soil met the CCME guidelines for both chrysene and B[a]P; whereas soil treated with either EDTA or control solution still contained high levels of B[a]P (60 μg g^{-1} in control residual and 46 μg g^{-1} in EDTA residual), although the remaining chrysene in all three treated soils was not detected. It is concluded that the optimized procedure with EDDS solution provides a promising technique for remediating soils that have been heavily contaminated with B[a]P and other higher-ringed PAHs.

By plotting the quantity of analyte (B[a]P or chrysene) that remained in the soil *vs.* the number of equilibrations, a decay curve for B[a]P or chrysene associated with the soil particulates fraction was obtained (Figure 3-22 and Figure 3-23). The y axis in Figure 3-22 represents the logarithm of the ratio of B[a]P remaining in the soil after N washes over the initial B[a]P concentration ($\ln[B[a]P]/[B[a]P_0]$). Similarly, y in Figure 3-23 represents the logarithm of the ratio of chrysene remained after N equilibrations over the initial concentration ($\ln[chry]/[chry_0]$). According to the first-order kinetic treatment, the relationship between B[a]P initial concentration ($[B[a]P]_0$) and the B[a]P that remained in the soil after N washes ($[B[a]P]_N$), and the number of washes (N = #W) can be expressed as:

$$-\Delta[B[a]P]_N/\Delta\#W = k[B[a]P_0] \qquad (1)$$

Where

#W = number of washes

k = constant of proportionality

$[B[a]P]_N$ = conentration in soil after N washes

$[B[a]P]_0$ = initinal concentration of B[a]P in soil

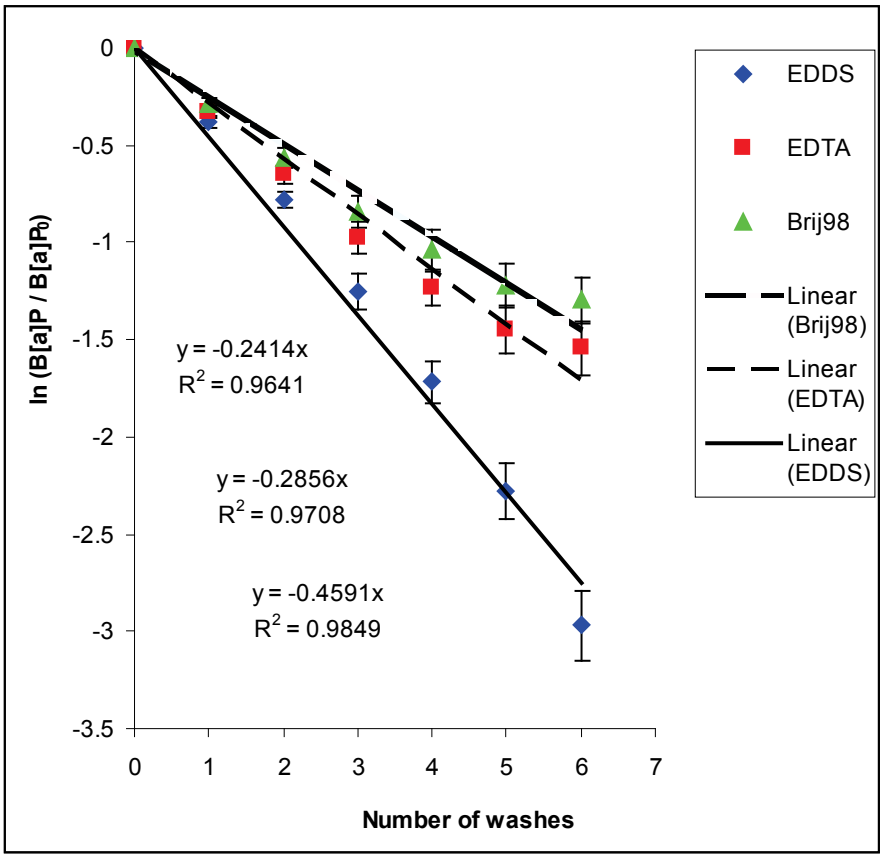


Figure 3-22. The decay curves of B[a]P remaining with the soil particulates fraction (ln of $B[a]P_N/B[a]P_0$) after sequential equilibrations with various washing solutions.

Equation (1) can be transformed to:

$$\ln([B[a]P]_N/[\ [B[a]P]_0) = k\#W \qquad (2)$$

Consequently, the following equation can be obtained from (2):

$$\#W_{1/2} = \ln 2/k \cong 0.693/k \qquad (3)$$

Where, $\#W_{1/2}$ = the number of washes needed to decrease the initial concentration of B[a]P by half. Equation (3) can also be used to predict the number of washes needed to reduce the initial concentration of chrysene by half.

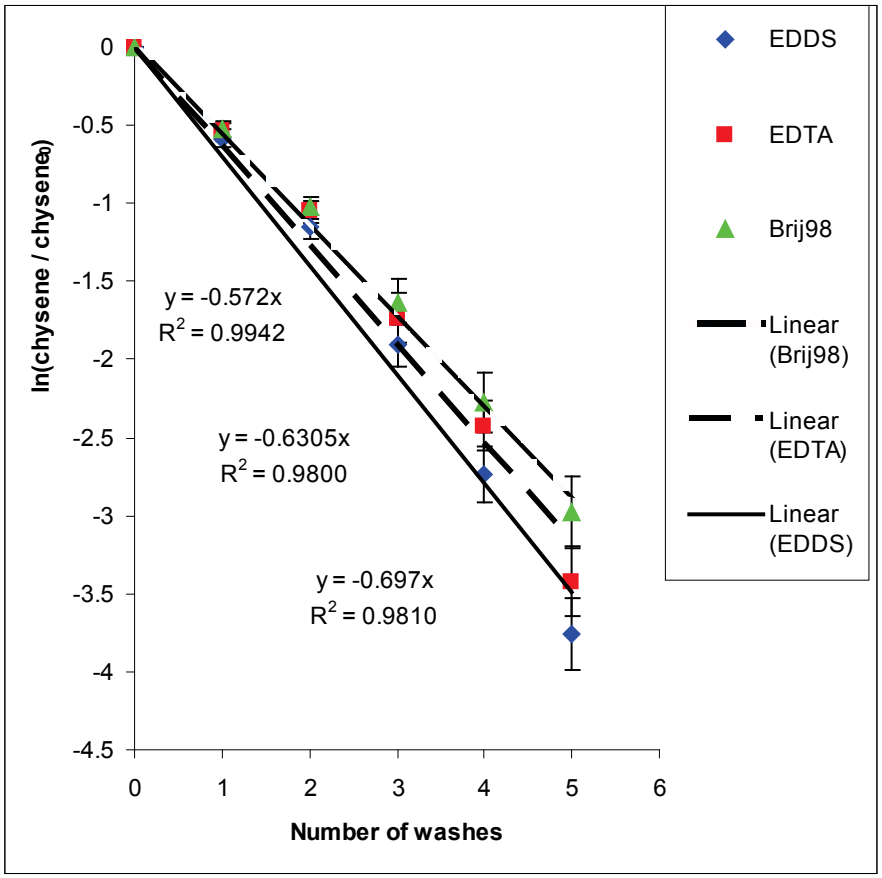


Figure 3-23. The decay curves of chrysene that remained with the soil (ln of ratio of $chrysene_N/chrysene_0$) after equilibrations with various washing solutions.

The values of k and $W_{1/2}$ of B[a]P and chrysene with various washing solutions are summarized in Table 3-14. To decrease B[a]P initial concentration in the soil by half, EDDS needed fewer equilibrations (1.5) than did EDTA (2.4) or Brij98 (2.9), which indicated that the mobilization efficiency in the presence of EDDS was higher at each equilibration and thus the washing process was more efficient in comparison

with EDTA or with Brij98. For chrysene mobilizations, the differences between the three predicted numbers of washes ($\#W_{1/2}$) were not appreciable (1.0, 1.1, and 1.2 for EDDS, EDTA and Brij98 respectively).

Table 3-14. The number of washes needed to reduce the total burden of B[a]P/chrysene by half with various reagent in mobilizing solution.

Reagent	B[a]P		Chrysene	
	k	$\#W_{1/2}$	k	$\#W_{1/2}$
EDDS	0.459	1.5	0.697	1.0
EDTA	0.286	2.4	0.630	1.1
Brij98	0.241	2.9	0.572	1.2

Tests for statistical significance (Table 3-15) based on the logarithmically transformed data, (B[a]P or chrysene removed from rather than remaining with the soil) revealed that the differences between EDDS-EDTA and EDDS-Brij98 on B[a]P mobilization were significant at the 95% level of confidence, whereas differences between EDTA and Brij98 were not significant. As to chrysene, all the three treatments were characterized by no statistically significant differences. In addition, the correlation analysis (Table 3-16) suggested that the mobilization of both compounds (B[a]P and chrysene) by all the three treatments were well correlated with the number of washing cycles. The cumulative metal mobilization after nine equilibrations with various washing solutions is presented in Table 3-17. The total mobilization of all twelve analyte metals by EDDS was 709 (μmoles g^{-1} soil), which was 1.7-fold greater than the total metal extraction (427μmoles g^{-1} soil) by EDTA and 2.8-fold greater than the total extracted (249 μmoles g^{-1} soil) by

surfactant. The differences in metal extractions among the three mobilizing solutions were mainly the result of differences in Fe mobilization. The EDDS solution mobilized 191 (μmole g^{-1} soil) more Fe than did the EDTA, and accounted for 68%

Table 3-15. Significant Test between various reagents on B[a]P and chrysene mobilization.

Compound	Reagents compared	Sample size (n)	t	$t_{0.01}$	$t_{0.05}$	Statistical Conclusion
B[a]P	EDDS EDTA	7	3.078	3.707	2.447	Significant (95 but not 99%)
	EDDS Brij98	6	3.664	4.032	2.571	Significant (95 but not 99%)
	EDTA Brij98	6	0.790	4.032	2.571	Not significant
Chrysene	EDDS EDTA	6	–1.480	4.032	2.571	Not significant
	EDDS Brij98	6	–1.118	4.032	2.571	Not significant
	EDTA Brij98	6	1.542	4.032	2.571	Not significant

of total difference (282 μmoles g^{-1} soil) between EDDS and EDTA. Similar results were observed between EDDS and surfactant: Fe difference between EDDS and surfactant made up to 70% of total difference (460 μmoles g^{-1} soil). Al was the second metal responsible for the appreciable differences, *i.e.* the differences of Al mobilization between EDDS-EDTA and EDDS-surfactant were up to 43% and 25% of total respectively. Ca was the next. EDTA mobilized the highest quantity of Ca

among all the three mobilizing solutions. Ca mobilization by EDTA was 25% and 48% more than the EDDS and the surfactant solution respectively.

Table 3-16. Correlation analysis between the number of washing cycles and PAH mobilization with various reagents.

Compound	Reagent	R	R^2
B[a]P	EDDS	–0.9981	0.9963
	EDTA	–0.9861	0.9724
	Brij98	–0.9772	0.9549
Chrysene	EDDS	–0.9968	0.9937
	EDTA	–0.9958	0.9915
	Brij98	–0.9968	0.9937

Based on the residue metals in the soil particulate fraction post washing, the three columns on the right in Table 3-17 provide a measure of the mean composition of the extracts. Fe comprised the highest percent of total metals extracted by each solution, Ca was the second and Al was the third.

The great degree of variations among Fe, Al, and Ca mobilization efficiencies with the various extracting solutions might help to explain the varied recoveries of B[a]P between EDDS, EDTA and surfactant. The total metal extracted by EDDS was 1.7-fold of the quantity extracted by EDTA, and was the result mainly to differences in Fe and Al extraction (Fe accounted for 68%; and Al for a further 43%). It might seem incongruous that the sum of the percent of Fe and Al exceeds 100. The reason for this is that the Ca increase by EDDS was negative (–12%, which decreased by 12% the total increase on metal extraction by EDDS). The soil organic matter

dissolution and B[a]P mass transfer from soil particulates into the EDDS aqueous solution was increased considerably. The same rationale can explain differences

Table 3-17. Metals mobilized from the soil.

	Metal mobilized from the soil (μmoles g^{-1} soil ± 1SD)			% of total extracted by each solution		
	EDDS	EDTA	Brij98	EDDS	EDTA	Brij98
Al	143±4	22±1	27±1	11	2.8	6.4
As	1.7±0.1	0.5±0.0	1.1±0.1	0.4	0.2	0.8
Ca	131±4	164±5	111±3	16	32	39
Cd	0.2±0.0	0.1±0.0	0.1±0.0	0.1	0.1	0.1
Cr	1.0±0.0	0.1±0.0	0.0±0.0	0.2	0.0	0.0
Cu	3±0.2	2±0.1	1±0.0	0.5	0.6	0.7
Fe	410±8	219±6	90±4	69	59	44
Mg	10±1	10±1	12±1	0.7	1.2	2.6
Mn	3±0.2	3±0.2	3±0.2	0.4	0.7	1.5
Ni	0.3±0.0	0.3±0.0	0.2±0.0	0.0	0.1	0.1
Pb	2±0.1	2±0.1	1±0.1	1.3	2	2.4
Zn	4±0.3	4±0.3	3±0.3	0.8	1.2	1.8
Σ_{HMs} (μmol)	**709**	**427**	**249**			

between EDDS and surfactant mobilization efficiencies. In the case of EDTA *vs.* surfactant, Fe mobilization differences were solely responsible for the increased B[a]P removal, because Al increase by EDTA was negative in comparison with surfactant and the increases in Cu and Pb extraction were negligible when compared with Fe.

Trace metals that remained within the soil particulates after nine soil washing cycles are presented in Table 3-18. Trace metals that remained with the soil particulate fraction were generally lower when EDDS had been included in the aqueous wash than if an equivalent of EDTA had been included and both were more efficient at mobilizing metals than was the surfactant alone. Residues of Cd, Cr, and Pb that remained after EDDS treatment were lower than the recommended maxima for industrial or commercial use, but exceeded the norms for agriculture and residential/parkland. In contrast, residues of these metals after treatment with EDTA

Table 3-18. Trace metals remained with the soil residual post nine soil washings.

	Metal residues remaining with the soil particulates (μg g^{-1} soil ± 1SD)			CCME[a] Guidelines (μg g^{-1} soil)			
	EDDS	EDTA	Brij98	Agr[b]	Resid[c]	Ind[d]	Comm[e]
As	226±15	318±20	269±22	12	12	12	12
Cd	13±1	26±3	27±3	1.4	10	22	22
Cr	82±5	128±9	132±11	64	64	87	87
Cu	374±22	434±35	482±37	63	63	91	91
Ni	37±3	39±3	41±3	50	50	50	50
Pb	205±11	216±20	354±32	70	140	600	260
Zn	136±10	141±11	181±15	200	200	360	360

[a.] Canadian Council of Ministers of the Environment (CCME), 2007 [135]. [b] permissible residues in soil destined for agricultural use; [c] permissible residues in soil destined for residential or parkland use [d] permissible residues in soil destined for industrial use; [e] permissible residues in soil destined for commercial use.

or surfactant frequently exceeded either all the legislative norms (Cd and Cr) or part of the permitted maxima (Pb). The residues of Ni and Zn after all three treatments were lower than all of the permitted limits, whereas Cu and As residues remained high after all the treatments, although the content in the particulates fraction after

EDDS treatment was 14% or 22% lower than after EDTA treatment or after surfactant treatment respectively.

3.5. Conclusion

Soil washing with a combination of a non-ionic surfactant and a complexing reagent has been demonstrated to extract mixed contaminants (heavy metals and PAH compounds). EDDS added to the surfactant solution, increased the recovery of B[a]P by 15% after five successive soil washes with the same charge of mobilization aids, *i.e.* 93% of total B[a]P was removed from the soil by 0.1 M EDDS-6% (V/V) Brij98 mobilizing solution, whereas control solution (that contained no [*S,S*]-EDDS) mobilized 78% of total soil burden. In contrast to B[a]P mobilization, chrysene recovery was not influenced appreciably by the presence of EDDS (recovery of treated was 4% higher than for the control solution). However, the recovery in the absence of EDDS was fairly high (93%) due to its relatively higher solubility in surfactant solution when compared with B[a]P. Perhaps the results suggested that chrysene might have been more loosely bound to the soil particles than B[a]P.

Studies that compared EDDS with EDTA revealed that EDDS was more efficient than EDTA at mobilizing both B[a]P and chrysene (8% higher for B[a]P and 9% for chrysene for a single wash at solution pH 9). Further, EDDS was more efficient at pH 9 than at pH 6 (6% difference for B[a]P and 5% for chrysene). In contrast, EDTA did not display any appreciable mobilization difference with respect to pH. The different behaviours between EDDS and EDTA for B[a]P and chrysene mobilization resulted from their different buffering capacities. EDDS possessed a

greater buffering capacity than EDTA and was more resistant to pH changes. As a result, the pH of soil suspension was maintained near the pH of the initial solution (prior to the addition of the very acidic (pH 3.5) soil). The increased buffering capacity of EDDS was beneficial when the initial pH of the mobilizing solution was high (pH 9). Alkaline pHs (~9) increased Fe and Al extraction from the oxidizable fraction and caused more DOM dissolution, which enhanced B[a]P and chrysene mass transfer from soil organic fraction into aqueous mobilizing solution.

The presence of EDDS in the surfactant solution also had a great influence on the mobilization of heavy and trace metals. Most analyte metals (Al, As, Cd, Cr, Cu, Fe, Ni, Pb and Zn,) were extracted more efficiently with solutions containing EDDS in comparison with solutions containing an equivalent quantity of EDTA or solutions in the absence of complexing reagent. By contrast, the mobilization of Ca, Mg, and Mn by EDDS was decreased when compared with EDTA and/or surfactant alone.

Process optimization studies indicated that pH, concentrations of the mobilization aids (EDDS and surfactant), duration of the ultrasonication stage and the solution/soil ratio all influenced both the B[a]P and chrysene mobilization as well as heavy and trace metal mobilization appreciably. The optimized conditions for the soil washing process were chosen as follows: 0.1 M EDDS in 6% (V/V) Brij98 adjusted to pH 9, 30 min of ultrasonication using a solution/soil ratio of 6.6.

During evaluation studies, the preferred washing solution (EDDS) was compared with two other washing formulations (EDTA- Brij98 or Brij98) under optimized conditions. The optimized procedure with EDDS mobilized a total of 101% of B[a]P

from the soil, which was 21% higher than that with the equivalent quantity of EDTA and 28% higher than extractions in the absence of complexing reagent (surfactant Brij98 alone). In addition, Modelling of the extraction process for PAH compounds remaining within the soil revealed that B[a]P was extracted more efficiently in the presence of EDDS, *i.e.* the number of washes needed to decrease the initial concentration of B[a]P by half was less than the predicted number of washes in the presence of either EDTA- Brij98 or Brij98, and the differences were significant at the 95% level of confidence. In contrast to B[a]P mobilization, the optimized procedure did not show any perceptible influence on chrysene removal when compared with EDTA or Brij98. The model decay curves displayed similar trends between the three mobilizing solutions when compared with the mobilization of B[a]P, *i.e.* EDDS solution removed slightly more chrysene than solutions containing EDTA or Brij98 alone, but the differences between EDDS-EDTA and EDDS-Brij98 were not statistically significant.

The total metal extracted by EDDS after nine equilibrations (with the same charge of mobilization aids) was 1.7-fold greater than total metal extraction by EDTA and 3-fold greater than the total extraction by surfactant. The differences were mainly the result of differences in Fe mobilization, which accounted for 68% of total difference between EDDS and EDTA, and 70% of total difference between EDDS and surfactant Brij98. Al was the second metal contributing to the differences (accounting for 43% and 25% of total differences between EDDS-EDTA and EDDS-surfactant respectively). The increased Fe and Al extraction by EDDS might

help to explain the increased degree of B[a]P mobilization, and also in turn reveals the correlation between Fe and Al extraction and B[a]P mobilization.

The residues of heavy and trace metals that remained with the soil particulates after nine sequential equilibrations with EDDS were generally lower than the metal residues that remained after EDTA treatment or Brij98 treatment. Residues of Cd, Cr, and Pb that remained after EDDS treatment were lower than the Canadian Council of Ministers of the Environment (CCME) guidelines for industrial and commercial use, but exceeded the maxima for use in agriculture and residential/parkland. In contrast, Cd and Cr residues after treatment with EDTA or surfactant exceeded all the legislative norms. The residues of Ni and Zn with all three treatments were lower than the recommended limits. Although Cu and As remained high after all the treatments, Cu residue by EDDS treatment was 14% and 22% lower than by EDTA and Brij98 treated soil residues; and arsenic (As) was decreased by 29% after EDDS treatments or 16% after the EDTA treatments when compared with the Brij98 washes.

In summery, the optimized soil washing procedure containing 0.1 M EDDS and 6% (V/V) Brij98 displayed increased mobilization efficiencies of mixed contaminants, PAH compounds and heavy metals. The findings are preliminary and need to be corroborated with further studies.

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